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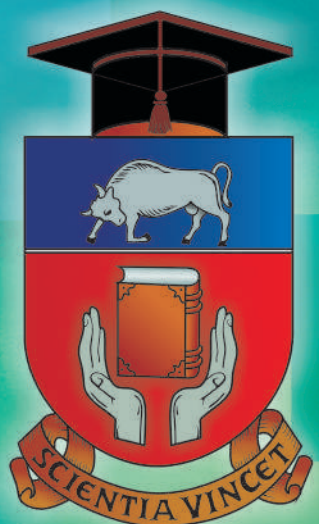
Nr.1 (13), 2022



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Processes and technologies applicable to the exploitation of non-wood forest products in the Republic of Moldova

Gheorghe Novac

Abstract. The aim of this research is to analyze the organization of the collection and processing of non-wood forest products in the Republic of Moldova. In order to achieve the goal, the following objectives were set: characterization of NWFPs harvesters, to establish and describe the technological processes applicable to the valorization of non-wood forest products; to analyze the organization of the collection and processing of non-wood forest products. The objectives were achieved through direct observations with NWFPs harvesters by conducting the questionnaire survey. The non-probability sampling technique used is called snowball sampling.
Keywords: non-wood forest products, colect, processing, technological processes.

Procedee și tehnologii aplicabile la valorificarea produselor forestiere nelemnoase din Republica Moldova

Rezumat. Scopul acestei cercetări constă în analiza modului de organizare a colectării și procesării produselor forestiere nelemnoase din Republica Moldova. Pentru îndeplinirea scopului s-au stabilit următoarele obiective: caracterizarea culegătorilor de PFNL, stabilirea și descrierea procedeelor tehnologice aplicabile la valorificarea produselor forestiere nelemnoase; analiza modului de organizare a colectării și procesării produselor forestiere nelemnoase. Îndeplinirea obiectivelor a fost efectuată prin observații directe cu culegătorii de PFNL, prin realizarea anchetei cu ajutorul chestionarului. Tehnica de eșantionare non-probabilistică utilizată, se numește eșantionarea în bulgăre de zăpadă.
Cuvinte cheie: produse forestiere nelemnoase, colectare, prelucrare, procese tehnologice.

1. Introduction

The forestry fund offers great opportunities for collecting, harvesting and processing non-wood forest products (NWFPs). The NWFPs exploitation process aims to supply consumers with good quality products throughout the year. In order to be satisfied with the work done and the income obtained from NWFPs exploitation, several steps have to be completed: harvesting, sorting, grading, packing, transporting, storing and selling. The application of efficient exploitation methods is also conditioned by the choice of

technological operations that ensure the shortest route to the consumer, thus ensuring that the quality of NWFPs is maintained.

A production-consumption system is defined as a whole set of goods, activities and entities involved in the processes of growing, harvesting, adding value and selling finished products. The system includes the technologies used, the production and processing activities, the social, economic and institutional environment in which the system operates [1].

Although the potential of the NWFP sector to reduce poverty and improve people's livelihoods is great, knowledge about the NWFP technology chain is insufficient. This process is individual, unorganized, dispersed and the participants lack sufficient knowledge to perform.

The proponents of promoting non-wood forest resources argue that harvesting and processing these products is a promising activity that can be undertaken without large investments [2].

For each species and plant organ, the following conditions are important when harvesting: the optimal time (time of year, time of day) for harvesting (which for most plants is the flowering period, or when the plant material contains the maximum amount of extracts with active substances) and the harvesting method (manual or mechanical, which aims to ensure that the material retains the maximum amount of extracts containing active principles) [3].

Although non-wood forest products are harvested in large quantities, up to 50% of the total volume is harvested, a situation caused by a shortage of labor, unsatisfactory remuneration, the long distance from the locality to the collection point, the lack of access roads [4]. In order to solve these problems, which also exist in the Republic of Moldova, it is proposed to develop schemes at the level of the forestry enterprise for determining the existing non-wood forest resources, forecasting the harvest, controlling and recording the quantities collected, applying an efficient technology, applying preferences to small business credit in the sector concerned.

NWFP processing significantly increases income and employment for low-income people around forests. The technical-material base necessary for the valorization of these products, in the Republic of Moldova, has experienced a degradation after the 1990.

In the process of organizing NWFP harvesting and processing, there are two closely interlinked and mutually dependent sides, the labor process and the technological process. The work process concerns the activity of harvesting and processing the products in question, and the technological process involves the quantitative and qualitative transformation of the harvested products. The quality of the product depends to a large extent on the

quality of the raw material, which in turn depends on how it is harvested and processed. Today, the organization of NWFP collection and processing is taking on new dimensions in the context of sustainable forest development. To this end, it is necessary to improve operating technology and compliance with legislation.

The NWFP value chain in the Republic of Moldova is a supply chain, represented by individuals and 13 legal entities [5].

The aim of this research is to analyze the organization of the collection and processing of non-wood forest products in the Republic of Moldova. In addition, there was carried out documentation and synthesis of knowledge on processes and technologies applicable to NWFP exploitation. This was fueled by the lack of scientific literature in Romanian on the subject

In order to achieve the goal, the following objectives were set: characterization of NWFP harvesters, establishment and description of technological processes applicable to the valorization of non-wood forest products; analysis of the organization of the collection and processing of non-wood forest products. The achievement of the objectives was carried out through direct observations with NWFP harvesters by conducting the questionnaire survey.

2. Methods and materials used

In the research process, depending on the stage of the investigation, several methods were used to collect, process data and organize information. According to the criteria for classifying research methods, in order to discover the relationships between different sides in the research carried out, there were used the cross-sectional method (survey), the quasi-experimental and observational method (survey, document study), statistical methods (opinion survey, mathematical-statistical analysis), methods of collecting information (statistical recording, survey), methods of processing information (quantitative and qualitative), methods of interpreting research data (comparative, interpretative).

For the practical study and further research, the main research method was the survey. The necessary primary data were obtained as a result of the field survey on a sample of 510 people. To this end, visits were made to 164 localities in 16 districts of the Republic of Moldova.

The research technique used was the questionnaire, the application procedure was individual-face-to-face, and the research instrument was the actual questions in the questionnaire.

NWFP harvesters in the study are represented by the rural population. Respondents answered an identical number of questions (31 questions) arranged on paper.

The questionnaire, being an investigative tool, included questions that elicited various responses from individuals. The response scales were based on a hierarchy of response variants, with choice answers, binary scales with dichotomous answers, scales with multiple answers; whenever necessary, the "I don't know" variant was also proposed.

Through coding, the responses from the questionnaires were converted into numbers and recorded electronically in Excel to facilitate further processing.

The sample size was calculated according to the formula [6, 7]:

$$n = \frac{t^2 * p\,(1-p) * N}{\Delta^2 * N - t^2 * p(1-p)};$$

where:

n – representative sample size;

t – coefficient associated with the probability of guaranteeing research results (value taken from statistical tables, usually $t = 1.96$ for $P = 95\%$);

p – incidence of the phenomenon ($p = 0.5$);

N – rural population size (1650300 persons, over 16 years old);

Δ - maximum permissible error ($\Delta \leq 0.05$);

$1 - p$ – probability of absence of the phenomenon.

$$n = \frac{1.96^2 * 0.5\,(1-0.5) * 1650300}{0.05^2 * 1650300 - 1.96^2 * 0.5\,(1-0.5)} = \frac{3.8416 * 0.5 * 0.5 * 1650300}{0.0025 * 1650300 - 3.8416 * 0.5 * 0.5} =$$

$$= \frac{1584948.12}{4125.75 - 0.9604} = \frac{1584948.12}{4124.7896} = 384.24 \approx 384\, persons.$$

The statistical processing of the primary information in the database was carried out using the application SPSS(R) („Statistical Package for the Social Sciences"), which takes into account that some variables are nominal and others are numeric.

The non-probability sampling technique used has been described in [8] and is called snowball sampling.

3. Results and discussions

The gender and marital status of respondents are basic characteristics in a survey. They describe women and men in terms of social status. Because of these particularities, people have different experiences, perceptions and attitudes towards the importance of NWFPs. These relationships between gender, marital status and NWFPs are determined by roles and responsibilities in family and society. The social particularities of NWFPs harvesters play an important role in the collection, use and distribution of NWFPs products. In the

result of the survey, 77% of the respondents were men and 23% were women. Of those interviewed 85% are married and 15% unmarried.

People's age influences attitude and interest in NWFPs. The age distribution of the surveyed harvesters is normal (Gaussian) according to the Kolmogorov-Smirnov test D=0.054. The arithmetic mean age of the sampled harvesters is m=45.8 years, with a root mean square deviation of SE=12.8. The age range of NWFPs harvesters is between 16 years (for the youngest) and 80 years (for the oldest). Estimates show that the majority of harvesters are between 25 and 62 years of age, and this is evidence of the importance of NWFPs to the population.

Interpreting the data on respondents' education, it was found that they graduated from different educational institutions (general education-36%, technical vocational-48% and higher education-16%). Regarding the occupation of harvesters, employees represent 57% and unemployed represent 32% of the sample. Retired harvesters are less numerous and represent 11%.

Before NWFPs harvesting begins, the areas with the given resources, potential and physiological maturity of the products to be harvested must be identified. It also prepares the inventory and storage location, identifies the workforce. Within a reasonable time, the harvesting plan and schedule for each species in each sector is drawn up, taking into account the overall production and the ripening period. An important aspect in the rational use of NWFPs is forecasting fruiting, which can be short or long term. Depending on the specifics and destination of the non-wood forest products, there are chosen the method of harvesting, inventory, loading/unloading and transport.

The methodology according to which the harvest is estimated is regulated by regulations and literature [9].

The determination of the optimum harvesting period depends on the method of harvesting, following assessment of the physical, biochemical or physiological changes occurring [10]. This avoids quantitative and qualitative losses [11].

The majority of harvesters (54%) rate NWFPs abundance as medium and 23% rate it as low. A smaller percentage of harvesters (17%) mentioned that the abundance of these products is high.

In the analysis carried out by the Institute of Forest Research and Management of the Republic of Moldova with reference to the area and the possibility of provisional harvesting of rosehip (Rosa canina L.) and hawthorn (Crataegus monogyna L.) from the forest fund, it is presented that the area of rosehip is 289921.3 ha, of hawthorn 77701.9 ha, and the quantity recommended for harvesting is 1283250 kg of rosehip and 22550 kg of hawthorn [12]. Comparing the existing areas of rosehip with those before the declaration

of Moldova's Independence, there has been a substantial increase, more than 100 times, while the commercial potential has increased only 17 times. For hawthorn, the same report is as follows: the area has increased 7 times and the commercial potential has remained practically the same.

The main non-wood forest products harvested by the population are: mushrooms, rosehip, lime blossom, walnuts, elderflower, St. John's wort, fruits of Cornus mas L., acacia flower, sloes, chamomile and wild garlic. The results obtained demonstrate that the most popular fruits harvested from the forest fund of the Republic of Moldova are the rosehip (Rosa canina L.), the forest horns (Cornus mas L.), the hawthorn (Crataegus monogyna L.), the aronia (Aronia melanocarpa Michx.-Elliott), the pigeon (Prunus spinosa L.). The main fruit and berry plantations in the forest background are aronia, the forest horns, less currant.

For the sustainable use of NWFPs, an important role is played by the way of collection. Harvesting by breaking is practiced by 65% of respondents. People who harvest non-wood forest products by felling represent 30% of the sample and 5% use other harvesting methods (e.g., shaking). These products must be ripe, clean, free of impurities, dry, fresh. An exception may be made for products which are intended for transport over longer distances, which can be collected and semi-collected. Green fruit and berries should not be picked, but stored and stored in cellars for ripening. It is also necessary to consider the collection period, which is important for their subsequent use. On hot days, it is recommended to harvest in the morning, after dew has been removed, and in the evening. Those picked at midday are not juicy enough and deteriorate quickly. Fruit and berries collected in wet weather deteriorate easily and rot, requiring urgent processing. In cold, gloomy weather, fruit and berries can be picked all day long. Harvesting is done every day or one day later, depending on weather conditions and market demand. The number of harvesters depends on the area and productivity of the plants, under the supervision of forestry staff, so as not to damage the fruit or plants.

Nut crops comprise two groups of species: coniferous and deciduous. For the forest fund of the Republic of Moldova, there are important those of the deciduous group (walnuts and hazelnuts). They have very low perishability, high dry matter content and can be stored for a long period of time without special rooms. Harvesting of walnuts begins in the first decade of September by shaking or falling by itself. It is not acceptable to break branches and green walnuts, because the kernel loses its qualitative and quantitative properties and cleaning is difficult. The ripening of walnuts coincides with the cracking of the mesocarp, when the kernel is fully developed. The ripening period of walnuts is gradual, therefore, in order not to harvest them in several rounds, they are shaken and

picked from the ground. Before harvesting walnuts, it is good to mow the grass to facilitate harvesting. Cleaning of mesocarp nuts is carried out at harvest time or at storage places. Cleaning can be done manually for small quantities or mechanically for larger quantities. If the mesocarp is not cleaned, the nuts are placed in dark, damp rooms (cellars) for several days and the mesocarp cracks. Walnuts should not be left for a long time in cellars for the mesocarp to crack, because it blackens and softens, then the walnuts wash harder and do not have an aesthetic appearance. After cleaning the mesocarp nuts, wash and dry in the sun. Walnuts should not be kept in water for a long time, as they soften the kernel and are difficult to dry out, creating conditions for mould to grow. Hazelnuts are harvested at the fully ripe stage, which can be visually established by the external changes that appear on the fruit. They are cleaned of impurities, spread in thin layers in the sun and dried.

Before starting to collect medicinal plants, it is necessary to distinguish them from the rest of the flora. There are several groups of medicinal plants, depending on the organ used: root, rhizome, tuber, bud, bark, leaf, flower, fruit, seed. Collection of the underground part is carried out in autumn after the end of the growing season or in spring until the beginning of the growing season. To help promote the species, it is advisable not to extract the entire root or, where it has been extracted, to sow seeds. The buds as raw material for medicinal products are collected from pine (Pinus sp.), spruce (Picea sp.), birch (Betula pendula Roth.), poplar (Populus sp.), blackcurrant (Ribes nigrum L.). The best time to harvest is in spring, when the buds are fully swollen and the leaves have not yet appeared. Buds are harvested only from trees to be removed in the logging process. Bark is harvested in spring, when sap circulation starts and is not affected by lichens. The vegetative part of medicinal plants is harvested in spring or summer, until flowering or during flowering. It can be cut with a knife, scissors, scythe or mechanical devices at the level of the last leaves. It is forbidden to extract the plant from the soil, as this affects the regeneration of the species and reduces its biological potential. Harvesting is recommended in dry weather, on cloudy days after the dew has evaporated. Leaves, depending on the species, are harvested at different stages of growth and development: during budding, flowering, fruiting. This process is carried out in dry weather. The leaves are broken from top to bottom. In some species, cut the shoots with scissors or a knife. The collected raw material is cleaned of impurities, leaves attacked by pests are removed, yellow leaves. Leaves can be harvested fresh directly from the plant or together with the plant after which they are dried and then harvested. The flowers or inflorescences of medicinal plants are harvested according to their flowering period. They are harvested by hand, or using various cutting tools or appliances. Flower picking is recommended at the beginning of flowering to avoid shaking. Before drying, the flowers are cleaned of any

impurities and unnecessary parts of the plant. Harvesting is done in alternating bands to ensure regeneration and perpetuation of the species. Ripe seeds and fruits are rich in therapeutic substances. Harvesting therefore takes place as they ripen. In some species, in order not to shake, cut the branches with partially ripe fruit, tie them in sheaves and hang them in a dry space. They are then shaken on a clean surface, where they are cleaned of impurities and placed in pots.

The best time to collect mushrooms is in the morning, when they are best seen due to the glow of dew drops. At this time of day, mushrooms are hardier, fresher and deteriorate less. The most practical and convenient method of picking mushrooms is by breaking them up, then cutting them with a knife and cleaning them of impurities on the spot or at the place of destination. It is better to harvest by cutting, so as not to destroy the mycelium and disturb the litter. Harvest only young mushrooms, leave old ones to reproduce mycelium. Although they fruit abundantly, wild mushrooms are not sufficient biological resources to be collected and processed in industrial quantities.

The researcher [13] mentions that the way of harvesting edible mushrooms does not influence the regeneration capacity.

At the same time as harvesting, presorting is carried out, which includes the removal of products and bodies which do not meet the storage conditions. Those destined for fresh processing should be harvested with stalks, in order to extend the shelf life, and those destined for processing can be harvested without stalks. In order to have a uniform rhythm in the harvesting process and to carry out quality control, it is recommended to harvest them in smaller areas, depending on the number of workers. Depending on the intensity of NWFPs ripening, harvesting can be total or selective, manual, mechanized or mixed.

Extensive research on NWFPs collection and consumption at European level was carried out in [14].

The distance travelled to NWFPs resources is an indicator that demonstrates the importance of the products for the population. The distance most harvesters (42%) travelled was 3 km, 30% travelled 5 km and 19% travelled 1 km. The fewest harvesters (7%) travelled up to 10 km to harvest NWFPs and 2% travelled more than 10 km.

After harvesting NWFPs are prepared for transport according to destination. Transport and handling of NWFPs account for a large share of total expenditure. During transport and handling the quality of the NWFP and packaging must be maintained. For this purpose, suitable means of transport and appropriate packaging must be used. The great diversity of NWFPs also imposes different requirements for transport and handling.

Perishable products require more special transport conditions, regarding temperature, humidity, while less perishable products can be transported by ordinary means of transport. NWFPs can be transported by land (road, rail, animal transport), sea and air, using the shortest and most appropriate routes, without stops.

Transport gives people more opportunities for mobility and development. This indicator measures the accessibility of the population to non-wood forest products for harvesting. When it comes to means of travel to harvest NWFPs, half of the harvesters interviewed (50%) went to harvest on foot, 21% went by car, 25% by wagon and only 4% went by bicycle. Harvested fruit and berries are transported to their destination unprocessed. It is not recommended to turn them over from one vessel to another as they deteriorate.

For transport, peanuts are packed in 50 kg bags. Each package shall be marked with labels indicating the name of the product, quality, year of harvest, weight, quality certificate number. After cleaning and drying, walnuts are sorted by size and colour, which are intended for sale, and those for the kernel need not be graded.

During transport of mushrooms, sun, dust and moisture should be avoided.

Given the climatic conditions of the area in which Moldova is located, with four seasons and a single harvest, the most common method used to preserve NWFPs was drying. The rudimentary (solar energy) and more sophisticated (temperature controlled) processes have been used. The results showed that 62% of the sample preferred to store NWFPs in dry form, clearly superior to canned (24%) or frozen (14%).

Fruits and berries can be canned, dried, frozen. From berries and wild berries, compotes, jams and syrups are prepared, which have a pleasant aromatic taste and are in demand on the market. The technological scheme for the preservation of fruit and berries includes the following operations: sorting, grading, washing, preparation of containers and lids, packing, filling, sterilization, sealing, completion, storage, sale.

Nut drying can be natural or artificial. After drying, walnuts are graded by size, divided into three categories: large, medium, small. Contaminated, empty, green nuts are not allowed. Nuts and hazelnuts should be kept in dry, ventilated and rodent-free containers.

Harvested medicinal plants shall be kept in dry, clean, dark and permanently ventilated rooms. Packed in sacks, paper boxes, cloth bags. Poisonous plants, containing essential oils, are kept separately, packed in hermetically sealed glass containers. The type of product, species, time and place of collection shall be indicated on each package.

According to current standards, mushrooms can be processed in different ways: dried, preserved, marinated and salted.

Processing of NWFPs is carried out to resist biodegradable factors, to extend shelf life and consumption. Several preservation processes are known: refrigeration, freezing,

drying, blanching, boiling [15], which are also applicable to NWFPs. Dried NWFPs have a low weight and volume and are easier to transport. They are packed in paper bags and kept in dry rooms. Drying of non-wood forest products can be artificial or natural. Direct sun-drying of the vegetative parts is not recommended, as chlorophyll is destroyed, the leaves turn brown and the nutrient content is greatly reduced. Fruits and underground parts of the plant can be dried directly in the sun. Smelly plants are separated from odourless ones so that the smell is not absorbed. If the drying temperature is not respected, the biological content of the products is destroyed. Proper processing of NWFPs increases their profitability, adds value to them, and improving and expanding knowledge in this area can increase production and facilitate the marketing of these products. Processing NWFPs helps preserve products, reduces losses and makes it easier for them to penetrate more distant markets.

Primary processing involves several operations: conditioning, harvesting, drying, shredding, transport, sorting, carried out with specialized machinery, through which the raw material is successively transformed, quantitatively and qualitatively, from its initial state into a finished product [3]. Regarding the prospect of using non-wood forest products the researcher [16] mentions that after processing their value increases by 4-20 times. This situation can also be seen on the market in the Republic of Moldova, where, for example, there are large price differences in the sale of medicinal plants [17].

According to the researcher [18] drying products is the healthiest solution for shelf life compared to frozen or canned products. This is also the opinion of NWFP harvesters in the Republic of Moldova, according to survey responses.

Purchasing points are also an important link in the production process, as this is where the quality of NWFPs is determined and where the aim is to collect/receive and produce as large quantities as possible. The author [19] demonstrates that the activity of purchasing non-wood forest products in the Tomsk region of the Russian Federation is a method of developing entrepreneurship in villages. The research carried out by [20] argues, from an economic point of view, the need to organize procurement networks in order to increase the involvement of NWFPs in the production of goods.

The creation or existence of NWFPs collection centres have a strategic role, as they guarantee the harvesters a safe place of realization and rhythmic supply for the internal or external market. The above activities may be subject to specialized or multi-functional stand-alone production capacity. At the same time, NWFPs traders will be able to buy various products from these centres. Regarding the information whether there is a collection point for non-wood forest products in the locality, it can be mentioned that 61%

of the respondents said that there is not, 18% of the sample answered that there is, and 21% said that they did not know.

Based on our own experience and making an analogy with the purchase of agricultural fruit, we have found that the successful organization of the activity of a purchasing point is determined by a series of technical-organizational measures, which are interdependent:

- Locate procurement points as close as possible to the source of NWFPs;
- Fitting out and equipping the purchasing points with the necessary items;
- Announcement in the area about the purchase of NWFPs;
- Accommodation and food for people coming to harvest from other areas;
- Daily or weekly remuneration of harvesters;
- Rapid dispatch of collected NWFPs to large purchasing points or directly to processors. Usually, in the Republic of Moldova, the points of purchase of non-wood forest products are forest cantons, through foresters or intermediaries.

The packaging technological operation is carried out in the packaging premises of the exploitation centres. Packing is the operation by which NWFPs are placed in containers, either haphazardly or arranged. The purpose of packaging is to maintain the integrity and quality of non-wood forest products during handling, transport, storage and to maintain an attractive appearance at the time of exploitation. Depending on the physical-chemical properties, quality and destination of non-wood forest products, several packaging methods are used: in bulk, by arrangement and semi-arrangement. Packing method is chosen according to species, perishability, destination and transport distance. Packaging involves choosing the most appropriate type of packaging, depending on the specific characteristics of the products. In order to identify the origin of the products, a label shall be affixed to the packaging giving information on the species, the producing unit, the quality and the date of packaging. Depending on the technological stage, packaging can be divided into: packaging for harvesting, packaging for transport, packaging for storage, packaging for internal and external fulfilment. They can be made of wood, cardboard, plastic, textiles, in order to ensure product quality. For perishable NWFPs it is recommended to use packaging without a lid. Harvesting in metal pots is not allowed as they oxidize and are no longer suitable for use. If the raw material contains ethereal oils, then it must be packed in tightly closed glass or metal containers with lids. The bark, root, leaves in the packaging process can be pressed, which guarantees better storage conditions and increases the packaging capacity. After packing, a label is placed in the pots, on which data on the name of the raw material, collection period, weight, place of harvesting, packing date and registration number are entered.

Packaging means the totality of the constituent elements in a functional complex, intended to contain or wrap a product or an assembly of products in order to ensure their quality and integrity during handling, transport, unpacking and consumption [21].

Storage consists of placing NWFPs for storage in various premises, called warehouses. The purpose of the stores is to ensure the preservation and maintenance of the quality of non-wood forest products. The choice of storage and storage method depends on the physical-chemical and physiological properties of the NWFPs. Storage can be in bulk or in packages. Prior to storage of NWFPs, storage facilities are cleaned, repaired, dried and disinfected. The packaged raw material is placed on shelves, grouped by category and stored according to product type. Rodents, which degrade the appearance of the raw material, must not enter the warehouses.

The majority of respondents (47%) go NWFPs picking with family and collect from the same places. As for solitary harvesters, they represent 35% of respondents and go alone to harvest NWFPs when abundance is low. Pickers who go picking with friends (12%) pick from the same place for recreational purposes. Those who go harvesting with people they know are a minority in the sample (6%) and non-wood forest products are mostly sold.

Previous studies [22, 23] have shown that value chains are sensitive to many factors: the nature of the product, the market in which it is sold, demand and supply factors. Studies on the stages of the NWFPs value chain have also been conducted by [24-26]. Although, the NWFPs sector is considered forward-looking, no one is contributing to the development of cultivation technology, this problem was also mentioned in [27].

A prerequisite for successful marketing of NWFPs is to market them in uniform batches, which must meet certain quality requirements. NWFP conditioning consists of a multitude of processes, used to prepare as required, depending on the final destination. Conditioning operations depend on the species, the technical and material equipment of the buying-in or sales centres and are provided for in various regulations. Conditioning can be mandatory, optional or excluded. The technological operations carried out in packaging are the following: loading, unloading, quantitative and qualitative reception, cleaning, sorting, grading, quality control.

4. Conclusions

The spread of NWFPs throughout the territory of the Republic of Moldova demonstrates the great potential of providing and solving the multiple requirements. Research and development of the NWFP technology chain is particularly important to enhance quality and bring them up to quality standards. The exploitation of NWFPs differs according to

species, location, processing and preservation of products. Technological process development contributes to sustainable supply of NWFPs by conserving resources, improving market value, increasing sales opportunities.

Due to the many-faceted technological process, the non-wood forest products sector in the Republic of Moldova involves a large number of people (about 23,000 people/year), of different ages, gender, education, as well as being a source of income, conclusions supported by the literature. Most people are involved in the collection of rosehips (around 15000) and linden blossom (around 2000).

NWFPs harvesting and processing technologies are relatively simple and readily available, and are known to people in resource areas. The main methods used to harvest non-wood forest products are by harvesting (65%) and felling (30%). This indicates that the population knows and respects the harvesting rules, with a positive effect on the protection and perpetuation of the species.

Primary processing by drying of NWFPs is preferred by most harvesters, direct buyers or exploitation centres. NWFPs consumed fresh have a lower number of technological elements compared to those processed dried, frozen or preserved.

Distance between NWFPs resources and harvesters influences the number of people, quantity harvested, effort expended and their performance.

The existence of collection points in the locality positively stimulates collectors to sell NWFPs.

The exploitation of NWFPs is also important because they are usually environmentally friendly, an important export commodity, and their cultivation can use some less productive land for tree plantations.

Due to increased interest in NWFPs, the amount harvested by the population increases and the biological potential of the plants decreases. This demonstrates that the haphazard harvesting of non-wood forest products has negative ecological consequences.

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Determination of the degree of helminth infestation of the ecaudate amphibians (the Anura: Ranidae, Bufonidae) depending on the biotic factors in conditions of the Republic of Moldova

Elena Gherasim, Dumitru Erhan, Viorica Coadă, and Ana Ţîganaş

Abstract. In this study is made an ecological analysis of the species composition, structure of the helminth community and the invasion degree of Ranidae and Bufonidae families in different habitats in Moldova. As a result, it has been established the presence of 17 helminths species. It was found that the diversity of helminth fauna of the studied amphibians is structured depending on the host species, biotop, biotic factors, gender and depending of the host onthogenesis. Thus, the greatest diversity of helminthes in amphibians in the family Ranidae was established in *Rana ridibunda* and *Rana lessonae* with 17 species, and for the species from the Bufonidae family, no different values were established, so each host species being infested with 3 species of helminthes.
Keywords: helminthological investigation, helminths, Ranidae, Bufonidae, Moldova.

Determinarea gradului de infestare cu helminți a amfibienilor ecaudați (Anura: Ranidae, Bufonidae) în dependență de factorii biotici în condițiile Republicii Moldova

Rezumat. În acest studiu se face o analiză ecologică a compoziţiei speciilor, structurii comunităţii de helminţi şi a gradului de infestare cu helminţi a amfibienilor din familiile Ranidae şi Bufonidae în diferite habitate din Moldova. Ca rezultat, sa stabilit prezenţa a 17 specii de helminţi. S-a constatat că diversitatea faunei helmintice a amfibienilor studiaţi este structurată în funcţie de specia gazdă, biotop, factorii biotici, gen, dar şi în funcţie de ontogeneza gazdei. Astfel, cea mai mare diversitate de helminţi la amfibienii din familia Ranidae s-a stabilit la speciile *Rana ridibunda* şi *Rana lessonae* cu 17 specii, iar pentru speciile din familia Bufonidae nu s-au stabilit valori distincte, astfel fiecare specie gazdă fiind infestată cu câte 3 specii de helminţi.
Cuvinte cheie: investigaţii helmintologice, helmminţi, Ranidae, Bufonidae, Moldova.

1. Introduction

It is known that the wild animals are an important source of parasites for humans and domestic animals.

The study of amphibian helminth fauna, the specificity of the circulation in the natural and anthropized biotopes and their contact with the host, allow the establishment of the parasitological situation, some characteristics in the pathogenesis of the formation of outbreaks of parasitic agents and the elaboration of measures with epizootic and epidemiological impact.

In addition to the faunal importance of the research, anurans are definitive hosts for several classes of helminthes, including Cestoda, Monogenea, Trematoda, Secernentea and Palaeacanthocephala [3-5, 7, 9-11, 13, 15, 16].

They also serve as intermediate hosts [2, 7, 8, 14-16] or as paratenic hosts [2, 3, 5,6, 9, 10, 13] for a wide variety of helminthes specific to the vertebrates. Therefore, helminth infracommunities (i.e., communities of parasite infrapopulations in a single host) are ideal systems for investigations of host responses to simultaneous parasitic infections and within-host interactions between co-infecting parasites.

Species of parasites in all of these groups may infect the host in different stages of the life cycles. Any specimen may be infected by more than one parasite simultaneously or at different times.

Therefore, several factors contribute to the dynamics and structure of parasite communities, such as seasonality, environmental heterogeneity or factors associated with the host, such as spatial distribution, population density, body size, age and host gender [1].

Obtaining and evaluating scientific data as a result of helminthological investigations on the species of ecaudata amphibians will elucidate their role as vectors of different groups of parasitic agents, but also the importance in the prophylaxis of helminthes specific to domestic, wild and company animals in conditions of the Republic of Moldova.

2. Materials and methods

Observing, collecting and obtaining data on the complex of anurans from *Ranidae* (*Rana ridibunda, R. lessonae, R. esculenta, R. temporaria, R. dalmatina*) and *Bufonidae* (*Bufo bufo, B. viridis*) families was performed in the center and south of Moldova.

All investigations regarding the study of the helminth fauna, the determination of the infestation degree by helminth of amphibian species was carried out in the laboratory of Parasitology and Helminthology of the Institute of Zoology.

Helminthological analysis was performed according to the standard method, which involves examination of all internal organs of the animal [22]. Helminthological investigations of the parenchymal organs were carried out with the help of compressors, and of the digestive tract - by successive washing.

The collection, fixation, determination and processing of the helminthological material was carried out according to the methods proposed by different authors [17-21, 23, 24]. After collecting, fixing and processing, the helminthological material was mounted using paraffin rings according to the method proposed by Seinhorst (1959). The helminthological material was determined according to contemporary methodology [22].

In order to quantify the characteristic of helminthes contamination, the intensity indexes (II, specimens) was calculated - the minimum and maximum number of parasites of a species and the extent of invasion (EI, %) - the percentage of host contamination by a parasite species.

Laboratory helminthological investigations of amphibian samples on the presence of helminthes or helminth elements (eggs, larvae) will contribute to obtaining data of great value in order to determine the importance of amphibians in the formation and maintenance of outbreaks of parasitic agents common to pets, domestic animals and wildlife.

3. Results and discussions

According to the helminthological investigations performed on amphibians from Ranidae and Bufonidae families in the center and southern area of the Republic of Moldova, the presence of 17 helminths species was established: *Haematoloechus variegatus* Rudolphi, 1819; *Codonocephalus urniger* Rudolphi, 1819; *Opisthioglyphe ranae* Froelich, 1791; *Paralepoderma brumpti* Buttner, 1951; *Prosotocus confusus* Looss, 1894; *Tylodelphys excavata* Rudolphi, 1803; *Diplodiscus subclavatus* Pallas, 1760; *Parastrigea robusta* Szidat, 1928, *Strigea falconis* Szidat, 1928; *Gorgodera varsoviensis* Sinitzin, 1905; *Haplometra cylindracea* Zeder, 1800; *Pleurogenoides medians* Olsson, 1876, *Cosmocerca ornata* Dujardin, 1845; *Oswaldocruzia filiformis* Goeze, 1782; *Icosiella neglecta* Diesing, 1851; *Spirocerca lupi* Rudolphi, 1809 *Acanthocephalus ranae* Schrank, 1788, which from a taxonomic point of view fall into 3 classes (Trematoda, Secernentea) (Trematoda, Secernentea, Palaeacanthocephala), 7 orders (Plagiorchiida, Echinostomida, Diplostomida, Ascaridida, Strongylida, Spirurida, Echinorhynchida), 16 families (Omphalometridae, Haematoloechidae, Plagiorchiidae, Lecithodendriidae, Gorgoderidae, Diplodiscidae, Diplostomatidae, Pleurogenidae, Diplodiscidae, Strigeidae, Macroderoididae, Cosmocercidae, Molineidae, Onchocercidae, Spirocercidae, Echinorhynchidae) and 17 genera (*Haematoloechus, Codonocephalus, Opisthioglyphe, Paralepoderma, Prosotocus, Gorgodera, Tylodelphys, Diplodiscus, Parastrigea, Strigea, Haplometra, Pleurogenoides, Cosmocerca, Oswaldocruzia, Icosiella, Spirocerca, Acanthocephalus*).

According to the analysis of the investigation performed, ***Rana ridibunda*** Pallas, 1771 was the species with the most helminth specimens investigated (n=45) and as a result, their infestation with 17 helminthes species was established, of which 12 species of trematods (*Opisthioglyphe ranae* Fröhlich, 1791, *Haematoloechus variegatus* Rudolphi, 1819, *Prosotocus confusus* Looss, 1894, *Diplodiscus subclavatus* Pallas, 1760, *Codonocephalus urniger* Rudolphi, 1819, *Paralepoderma brumpti* Buttner, 1951, *Pleurogenoides medians* Olsson, 1876, *Parastrigea robusta* Szidat, 1928, *Haplometra cylindracea* Zeder, 1800, *Gorgodera varsoviensis* Sinitzin, 1905, *Strigea falconis* Szidat, 1928, *Tylodelphys excavata* Rudolphi, 1803), 4 species of secernentea (*Oswaldocruzia filiformis* Goeze, 1782, *Cosmocerca ornata* Dujardin, 1845, *Icosiella neglecta* Diesing, 1851, *Spirocerca lupi* Rudolphi, 1809) and a species of the class Palaeacanthocephala (*Acanthocephalus ranae* Schrank, 1788).

For 13 of the 17 helminths species detected Rana ridibunda is the definitive host, and for 4 helminths species it is the paratenic host.

At helminthological investigation of the ***Rana lessonae*** species (n = 19), the presence of 17 helminths species was established too, of which 12 trematodes species (*Opisthioglyphe ranae* Fröhlich, 1791, *Haematoloechus variegatus* Rudolphi, 1819, *Prosotocus confusus* Looss, 1894, *Diplodiscus subclavatus* Pallas, 1760, *Codonocephalus urniger* Rudolphi, 1819, *Paralepoderma brumpti* Buttner, 1951, *Pleurogenoides medians* Olsson, 1876, *Parastrigea robusta* Szidat, 1928, *Haplometra cylindracea* Zeder, 1800, *Gorgodera varsoviensis* Sinitzin, 1905, *Strigea falconis* Szidat, 1928, *Tylodelphys excavata* Rudolphi, 1803), 4 species of secernentea (*Oswaldocruzia filiformis* Goeze, 1782, *Cosmocerca ornata* Dujardin, 1845, *Icosiella neglecta* Diesing, 1851, *Spirocerca lupi* Rudolphi, 1809) and a species of the class Palaeacanthocephala (*Acanthocephalus ranae* Schrank, 1788).

For 13 of the 17 helminthes species detected *Rana lessonae* is the definitive host, and for 4 helminthes species it is the paratenic host.

In ***Rana esculenta*** (n=16) the presence of 12 species of helminths was determined, of which 8 species of trematodes (*Opisthioglyphe ranae* Fröhlich, 1791, *Haematoloechus variegatus* Rudolphi, 1819, *Gorgodera varsoviensis* Sinitzin, 1905, *Prosotocus confusus* Looss, 1894, *Diplodiscus subclavatus* Pallas, 1760, *Codonocephalus urniger* Rudolphi, 1819, *Pleurogenoides medians* Olsson, 1876, *Tylodelphys excavata* Rudolphi, 1803), 3 species of secernentea(*Oswaldocruzia filiformis* Goeze, 1782, *Cosmocerca ornata* Dujardin, 1845, *Icosiella neglecta* Diesing, 1851) and a species of the class Palaeacanthocephala (*Acanthocephalus ranae* Schrank, 1788)

For 9 of the 10 helminthes species detected *Rana esculenta* is the definitive host, and for one helminthes species it is the paratenic host.

According to the helmintological investigations carried out at the ***Rana dalmatina*** species (n = 12) the presence of 5 species of helminthes was established, of which 3 species of trematodes (*Opisthioglyphe ranae* Frölich 1791, *Haematoloechus variegatus* Rudolphi 1819, *Parastrigea robusta* Szidat, 1928) and 2 species of secernentea (*Oswaldocruzia filiformis* Goeze, 1782, *Cosmocerca ornata* Dujardin, 1845). At 4 of the 5 species of helminthes detected, *Rana dalmatina* is the definitive host, and for one species it is the paratenic host.

The amphibian species from the family Bufonidae - ***Bufo bufo*** (n = 30) and ***Bufo viridis*** (n = 11) the presence of 3 species of helminthes was determined each, of which 2 species of nematodes (*Oswaldocruzia filiformis* Goeze, 1782, *Cosmocerca ornata* Dujardin, 1845) and a species of acanthocephalus (*Acanthocephalus ranae* Schrank 1788), for which these serve as definitive hosts.

In order to quantify the characteristic of helminth contamination detected in amphibian species of the families Ranidae and Bufonidae, the main parasitological indices were calculated which include the minimum and maximum number of parasites of one species (II, specimens) and the percentage of contamination for each host species with each helminth species (EI,%) Table 1.

At the same time, the helminthological researches, depending on the host ontogenesis were performed, and in order to carry out this research, the amphibians from two age categories were helminthologically investigated: adults and juveniles.

Thus, 17 juveniles of *Rana ridibunda* species were helminthologically investigated, in which the presence of 4 species of helminthes was established, of which 3 species of trematodes (*Opisthioglyphe ranae* Fröhlich, 1791, *Haematoloechus variegatus* Rudolphi, 1819, *Diplodiscus subclavatus* Pallas, 17) and a species of secernentea (*Cosmocerca ornata* Dujardin, 1845).

The results of the researches allow us to conclude that with the increase of the size and age of the amphibians, the degree of helminthes infestation also increases. This peculiarity demonstrates the intensification of the diet of adult amphibians and the accumulation of parasitic agents in their body, as well as increasing the size and diversity of foods that promote the simultaneous penetration of more parasitic agents into the host body, leading to increased infestation.

Therefore, according to the results of the helminthological research obtained, it was established that the diversity of helminthes and their infectivity is higher in amphibians

in floodplain lakes with relatively constant environmental conditions. Amphibians from anthropized aquatic habitats with dynamic environmental conditions are less infected

Table 1. Infection level of ecaudata amphibians from Ranidae and Bufonidae families

Nr.	Host	*Rana ridibunda n=45*		*Rana lessonae n=19*		*Rana esculenta n=16*		*Rana dalmatina n=12*		*Bufo bufo n=30*		*Bufo viridis n=11*	
	Invasion	**II, ex.**	**EI, %**	**II, ex.**	**EI, %**	**II, ex.**	**EI, %**	**II, ex.**	**EI, %**	**II, ex.**	**EI, %**	**II, ex.**	**EI, %**
TREMATODA													
1.	*O. ranae*	1-114	88.9	1-94	73.7	1-64	87.5	1-23	66.7	-	-	-	-
2.	*H.variegatus*	1-5	75.6	1-3	10.5	1-4	18.8	1-3	50.0	-	-	-	-
3.	*G.varsoviensis*	1-3	22.2	1-2	15.8	1	18.8	-	-	-	-	-	-
4.	*P. confusus*	1-98	80.0	1-111	63.2	1-46	56.3	-	-	-	-	-	-
5.	*D.subclavatus*	1-15	86.7	1-15	89.5	1-11	25.0	-	-	-	-	-	-
6.	*C.s urniger*	1-63	22.2	1-6	36.8	1-11	25.0	-	-	-	-	-	-
7.	*P.brumpti*	1-21	6.8	1-26	57.9	-	-	-	-	-	-	-	-
8.	*P.medians*	1-43	17.8	1-32	31.8	1-6	56.3	-	-	-	-	-	-
9.	*S. falconis*	1-14	22.2	1-31	42.1	-	-	-	-	-	-	-	-
10.	*P. robusta*	1-55	22.2	1-8	42.1	-	-	1-11	83.3	-	-	-	-
11.	*T. excavata*	1-228	88.9	1-187	57.9	1-114	87.5	-	-	-	-	-	-
12.	*H. cylindracea*	1-28	75.6	1-21	36.8	-	-	-	-	-	-	-	-
SECERNENTEA													
13.	*O. filiformis*	1-4	24.4	1-3	15.8	1-7	87.5	1-3	41.7	1-28	83.3	1-27	54.5
14.	*C. ornata*	1-10	86.7	1-3	52.6	1-19	87.5	1-6	66.7	1-27	60.0	1-133	81.8
15.	*I. neglecta*	1-5	26.7	1-9	26.3	1-13	37.5	-	-	-	-	-	-
16.	*S. lupi*	1-98	53.3	1-70	57.9	-	-	-	-			-	-
PALAEACANTHOCEPHALA													
17.	*A. ranae*	1-4	11.1	1-2	26.3	1-4	37.5	-	-	1	26.7	1-2	27.3

with the same diversity of species; they are characterized by a relatively small number of helminthes species and a low level of helminth invasion.

The causes of differences in amphibian infestation by helminthes in different biotopes are complex. Diversity, high abundance of mollusks and arthropods (intermediate, definitive, paratenic hosts) cause a high level of infestation of amphibians with transmission through food chains. The high density of the amphibians themselves, and, accordingly,

of the predators batrachophages, leads to intensive infestation of frogs by larval stages of helminthes.

4. Conclusions

(1) The helminth fauna of 133 specimens of ecaudata amphibians (Ranidae, Bufonidae) was studied from Central Forest (Codrii Reservation, Ciuciuleni village) and in the natural ecosystem - the Dniester River, from the village of Talmaza from the Stefan-Voda district.

(2) It has been established the presence of 17 helminths species: *Haematoloechus variegatus* Rudolphi, 1819; *Codonocephalus urniger* Rudolphi, 1819; *Opisthioglyphe ranae* Froelich, 1791; *Paralepoderma brumpti* Buttner, 1951; *Prosotocus confusus* Looss, 1894; *Tylodelphys excavata* Rudolphi, 1803; *Diplodiscus subclavatus* Pallas, 1760; *Parastrigea robusta* Szidat, 1928, *Strigea falconis* Szidat, 1928; *Gorgodera varsoviensis* Sinitzin, 1905; *Haplometra cylindracea* Zeder, 1800; *Pleurogenoides medians* Olsson, 1876, *Cosmocerca ornata* Dujardin, 1845; *Oswaldocruzia filiformis* Goeze, 1782; *Icosiella neglecta* Diesing, 1851; *Spirocerca lupi* Rudolphi, 1809; *Acanthocephalus ranae* Schrank, 1788, which from a taxonomic point of view fall into 3 classes (Trematoda, Secernentea, Palaeacanthocephala), 7 orders (Plagiorchiida, Echinostomida, Diplostomida, Ascaridida, Strongylida, Spirurida, Echinorhynchida), 16 families (Omphalometridae, Haematoloechidae, Plagiorchiidae, Lecithodendriidae, Gorgoderidae, Diplodiscidae, Diplostomatidae, Pleurogenidae, Diplodiscidae, Strigeidae, Macroderoididae, Cosmocercidae, Molineidae, Onchocercidae, Spirocercidae, Echinorhynchidae) and 17 genera (*Haematoloechus, Codonocephalus, Opisthioglyphe, Paralepoderma, Prosotocus, Gorgodera, Tylodelphys, Diplodiscus, Parastrigea, Strigea, Haplometra, Pleurogenoides, Cosmocerca, Oswaldocruzia, Icosiella, Spirocerca, Acanthocephalus*).

(3) It was found that the diversity of helminth fauna of the studied amphibians is structured depending on the host species, so the greatest diversity of helminthes in amphibians in the family Ranidae was established in *Rana ridibunda* and *Rana lessonae* with 17 species, and the lowest diversity in *Rana dalmatina* species - with 5 species of helminths, and for the species from the Bufonidae family, no different values were established, so each species being infested with 3 species of helminthes.

(4) It was determined that the helminth fauna of the amphibians investigated according to the age of the host shows divergent values, so that in the juveniles of the

Rana ridibunda species there was established the infestation with only 4 species of helminthes.

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Actual applications of infrared spectrophotometry in determining the quality of daily products

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Abstract. Fourier transform infrared spectroscopy (FTIR) is a fast and non-destructive analytical method. Combined with chemometrics, it is a powerful tool for the pharmaceutical, cosmetics and food industries. This method can be used for qualitative and quantitative analysis of medicines, foods and other daily products. At the same time, IR spectroscopy is becoming a suitable technique in the processes of drug preparation and for monitoring the productive processes in quality control laboratories. In this paper, IR spectroscopy is used to determine the concentration of alcohol in hand sanitizers, which is essential for slowing the spread of viruses. The effectiveness of hand sanitizer is entirely determined by the volatile ingredient, alcohol, which must remain at a concentration greater than 60% (volume) to destroy bacterial and viral pathogens. The selected samples varied according to the initial concentration of ethyl alcohol, manufacturer, color, perfume and other ingredients, as well as the validity period.
Keywords: ethanol, hand sanitizer, infrared spectroscopy, standard addition, expiration date.

Aplicații actuale ale spectroscopiei în infraroșu în determinarea calității unor produse cotidiene

Rezumat. Spectroscopia în infraroșu cu transformată Fourier (FTIR) este o metodă analitică rapidă și nedistructivă. Asociată cu chimiometria, este un instrument puternic pentru industria farmaceutică, cosmetică și alimentară. Această metodă poate fi utilizată pentru analiza calitativă și cantitativă a medicamentelor, alimentelor și a altor produse utilizate în cotidian. Totodată, spectroscopia IR poate fi utilizată în timpul preparării medicamentelor și pentru monitorizarea procesului de producție în laboratoarele de control al calității. În lucrarea de față, spectroscopia IR este utilizată pentru determinarea concentrației de alcool în dezinfectantele pentru mâini, acesta fiind esențial pentru încetinirea răspândirii virusurilor. Eficacitatea dezinfectantului pentru mâini este în întregime determinată de ingredientul volatil, alcoolul, care trebuie să rămână la o concentrație mai mare de 60% (volum) pentru a ucide agenții patogeni bacterieni și virali. Probele de dezinfectant pentru mâini selectate, au variat după concentrația inițială de alcool etilic, producător, culoare, parfum și alte ingrediente, precum și termenul de valabilitate.
Cuvinte cheie: etanol, dezinfectant pentru mâini, spectroscopia în infraroșu, adăugare standard, date de expirare.

1. Introduction

Infrared spectroscopy (IR) is certainly one of the most important analytical techniques available to scientists [1]. Being an improved method over time, at present, it allows the practical study of different types of samples [2]. The major advantage of IR spectroscopy over other spectroscopic techniques is that all the compounds virtually have absorption (emission) and thus can be analyzed both qualitatively and quantitatively [3].

Fourier-transform infrared spectroscopy (FTIR) was originally a spectroscopic technique used to identify the functional groups of chemical substances, but in recent years it has been widely used to identify, control quality and monitor the manufacturing process of drugs [3], assess the quality of agricultural products, in particular foodstuffs [4], as well as in the field of forensics for the identification of traces and fingerprints [5].

The principle of IR spectroscopy is to measure the amount of IR radiation that is absorbed (or emitted) by a sample as a function of wavelength [3]. IR spectrum measurement can be performed in transmission or reflectance mode, the former being the most popular. This method is easy to use in the analysis of pharmaceutical, food, and cosmetic components because it often requires minimal preparation or even testing of the unprepared sample. This paper represents one of the areas of the use of IR spectroscopy, namely how to use IR spectroscopy to determine the concentration of alcohol in hand sanitizers.

Ethanol or isopropyl alcohol with the concentration of 60-95% (volume) is an active ingredient in all alcohol-based hand sanitizers. The given ethanol concentration has been tested and shown to be effective against common bacteria, including Serratia marcescens, Pseudomonas aeruginosa, Escherichia coli, Salmonella typhosa, Staphylococcus aureus, and Streptococcus pyogenes [6, 7]. In the presence of ethanol, the hydrophobic forces that keep the cell membrane intact are weakened because ethanol is less polar than water, causing an increase in membrane permeability and leakage of life-sustaining intracellular components [8]. It is important to note that 60% alcohol is the lowest concentration that remains effective against these common bacteria, however, 100% alcohol is ineffective against Staphylococcus aureus and Streptococcus pyogenes, as high alcohol concentration will cause clotting of the peptidoglycan layer, which protects bacteria from further damage [9].

In terms of viral pathogens, the usual hand sanitizer with 60-80% ethanol is effective against protein capsid viruses, such as coronavirus. Concentrations greater than 60-95% are required for efficacy against non-encapsulated viruses, such as poliovirus and adenovirus [10].

Law enforcement agencies, which are responsible for detaining inefficient products, need a reliable and practical method of determining the ethanol content in hand sanitizer to assess whether the amount of ethanol matches the value indicated on the ,,product label".

Several techniques are known to measure the ethanol concentration, including redox titrations [11], flow injection electroanalytical analysis [12], amperometric biosensors [13], and gas chromatography coupled mass spectrometry [14]. Although effective, these techniques take a long time, extensive preparation, and are destructive to the sample. That is why Fourier transform (FTIR) infrared spectroscopy (FTIR) was chosen for this study, being accessible, easy to use, and with high accuracy.

Figure 1. Hand sanitizer samples examined and 20 ml ampoules with diluted hand sanitizer solution.

When determining the concentration of ethanol in water, it is important to consider the similarities between the two molecules. Both can form hydrogen bonds due to the presence of hydroxyl groups, however, ethanol has a carbon-oxygen bond that can be identified using FTIR and is displayed at 1044-1045 cm^{-1} in the transmission spectrum [15]. This methodology of using the C-O bond was used by ,,FTIR manufacturers Perkin Elmer and Shimadzu to determine the efficiency of estimating the percentage of ethanol in hand sanitizer solutions" [16, 17]. Both studies are based on the calibration curve technique, preparing samples with high ethanol concentration based on WHO (World Health Organization) guidelines for hand sanitizer, using water as a control sample [18, 19]. This approach can produce a matrix effect in which the analytical signal is altered due to a non-analyte component of the hand sanitizer.

The study aims to determine the concentration of alcohol in a series of hand sanitizers (Figure 1). The concentration of alcohol in the nominated hand sanitizers was determined by the method of standard additions of known concentration of ethyl alcohol, to the diluted

sample of hand sanitizer and monitoring the change in the intensity of the C-O band in the alcohol.

2. Materials and methods

Materials: 70% ethyl alcohol was purchased from LUXFARMOL SRL (product code 220890910). Four samples of hand sanitizers with different expiration dates, were purchased (Figure 1): (A) Septophan, 65-75% (02.2021) - blue liquid; (B) Compact, 73% (10.2022) - transparent gelled solution; (C) Ecco, 75% (04.2025) - blue liquid; (D) Vitanic, 70% (09.2023) - colorless liquid. To prevent evaporation of the alcohol, the sample vials were covered throughout the experiment.

Table 1. Addition of standard to A-D hand sanitizer samples

Sample	Hand sanitizers information	Dilute Samples	V_o (ml)	V_t of ethanol in V_o , ml	V_s, ethanol, ml	V (ml)	$I_{(s+x)}$	$C_i \cdot V_s / V_0 \cdot 100$	$I_{(s+x)} \cdot V / V_0$
A	70%, 02.2021	A1	13.0	3.5	0	13	1057.72	0.000	1057.72
		A2	13.0		1	14	1138.50	0.054	1226.08
		A3	13.0		2	15	1179.76	0.107	1361.27
		A4	13.0		3	16	1246.44	0.161	1534.09
		A5	13.0		4	17	1285.89	0.215	1681.56
B	75%, 10.2022	B1	13.0	3.75	0	13	1179.27	0.000	1179.27
		B2	13.0		1	14	1305.88	0.054	1406.33
		B3	13.0		2	15	1378.32	0.107	1590.38
		B4	13.0		3	16	1442.45	0.161	1775.32
		B5	13.0		4	17	1462.44	0.215	1912.42
C	73%, 04.2025	C1	13.0	3.65	0	13	1163.44	0.000	1163.44
		C2	13.0		1	14	1216.62	0.054	1310.21
		C3	13.0		2	15	1279.96	0.107	1476.88
		C4	13.0		3	16	1322.71	0.161	1627.95
		C5	13.0		4	17	1369.88	0.215	1791.39
D	70%, 09.2023	D1	13.0	3.5	0	13	1061.68	0.000	1061.68
		D2	13.0		1	14	1174.50	0.054	1264.85
		D3	13.0		2	15	1262.48	0.107	1456.71
		D4	13.0		3	16	1344.50	0.161	1654.78
		D5	13.0		4	17	1400.44	0.215	1831.35

Preparation of A-D samples and addition of standard: 5 mL of sample (hand sanitizer) were pipetted to a 20 mL vial with a stopper. To the given sample 8 mL of distilled water was added, and the closed vial with a sieve was stirred gently (sample A). We note the initial sample of diluted hand sanitizer as "A1.....", A - the letter corresponding to the sample. The background spectrum of the diluted sample A1 (without the addition of ethyl alcohol) was measured. By the method of successive additions, by adding 1 mL of ethanol (70%), samples A2-A5 were prepared, measuring the IR spectra of the sample, after each addition of the standard. Samples B, C, and D were treated similarly.

IR Spectroscopy: The QUART-S Spectrophotometer was used for measurements. A background scan was initially performed to calibrate the spectrophotometer. One or two drops of sample A were transferred to the IR diamond crystal of the spectrometer. An IR spectrum of the sample was generated, performing 15 scans. The IR range was set at 4000-600 cm^{-1}.

For each sample investigated, IR spectra were measured. From the obtained IR spectra, there was documented the area of the band in the region 1044-1045 cm^{-1}, which corresponds to the C-O bond in the alcohol. Analyzing the changes in intensity in the IR spectrum of the samples, which appeared with each addition of ethyl alcohol, the graph was constructed: $[C]_i \cdot V_s / V_0$] as a function of $I_{(s+x)} \cdot V/V_0$ for the samples A-D, where V_0 – the initial volume of a dilute solution (13 ml); V_s – the volume of added ethanol (standard); V - the total volume of the solution; $I_{(s+x)}$ - the absolute value of the peak area at each addition of the standard (band area); C_i - initial alcohol concentration (standard).

3. Results and discussions

In this study, we presented data on alcohol concentration in four hand sanitizer samples, with different expiration dates (Table 1). The five solutions of each hand sanitizer samples were prepared by dilution and successive addition of standard. Five measurements were performed and the change in the intensity of the C-O band corresponding to the primary alcohols was analyzed. The absolute value of the peak area at each standard addition (C-O band area) was calculated using the LabSolutions IR program and noted in Table 1, Figure 2.

Using the calibration curve obtained by adding the standard (Figure 3) the initial alcohol concentration in hand sanitizers was calculated. The point of the intersection of the line with the **x** - axis, represents the initial concentration $[X]_i$ of the alcohol in each sample of hand sanitizer. The initial sample has the volume of 5 mL. It was diluted with water to reduce its viscosity, the final volume being noted in Table 1. Using equation (1), we can

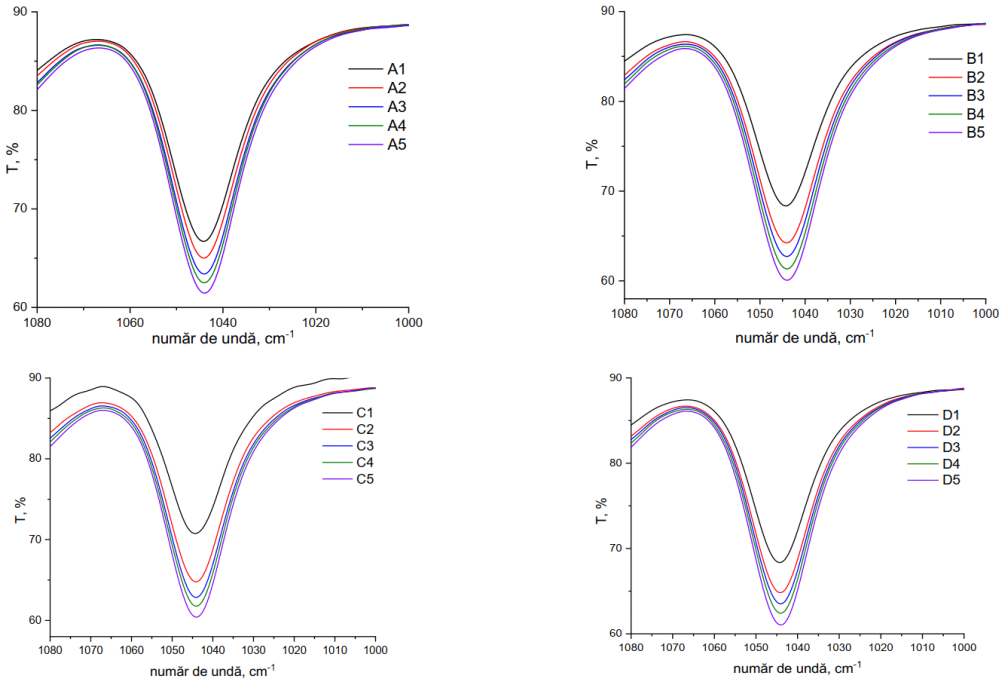

Figure 2. IR spectra of the studied samples A-D, indicating the region of interest, 1080-1000 cm^{-1}

calculate V_e the experimental volume of ethanol in 5 mL of hand sanitizer.

$$V_e = (13 \cdot [X]_i) / (1 + [X]_i) \quad (1)$$

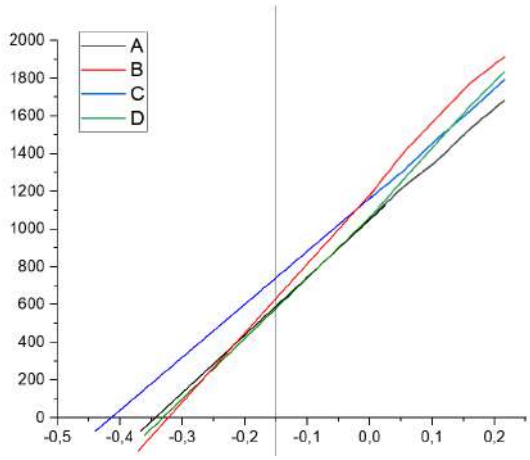

Figure 3. Calibration curve for A-D samples

The calculated volume of alcohol in the investigated hand sanitizers is shown in Table 2.

Table 2. Volume of ethanol determined experimentally for A-D samples

Sample	$[X_i]$ C_2H_5OH in 13 ml sample (%)	% (volume) C_2H_5OH, obtained	% (volume) C_2H_5OH, indicated	Loss of C_2H_5OH, % (volume)
A	0.344	66	70	6
B	0.323	63	73	14
C	0.413	75	75	0
D	0.331	60	70	15

The hand sanitizer "Sample A" expired two months ago, and the amount of ethanol identified is 66%, which is a loss of about 3% per month. However, the "Sample A" hand sanitizer remains effective, as the amount of alcohol detected is > 60%. In the hand sanitizers "Sample B" and "Sample D", which have not been yet expired, revealed a loss of volume of ethanol of 14% and 15%, respectively, which allowed us to conclude that they initially had a lower alcohol concentration than indicated on the package. The concentration of alcohol in "Sample C" proved to be equal to that indicated on the package, so we can conclude that the initial concentration of alcohol in this hand sanitizer was higher than that indicated on the package, taking into account the volume losses in time.

4. Conclusions

Infrared spectroscopy, compared to traditional methods, is one of the most efficient, easy, and inexpensive methods of qualitative and quantitative analysis of pharmaceutical, food, and industrial samples. This study demonstrated the effectiveness of using IR spectroscopy to determine the ethanol concentration in the samples. The alcohol concentration was determined using the calibration curve obtained by adding the standard, considering the matrix effect. While expired "Sample A" may still be effective, with the minimum threshold for ethanol in hand sanitizers being 60% (volume), "Sample C" suggests that manufacturers may use a higher percentage of alcohol to create hand sanitizer, thus maintaining the effectiveness and avoiding the loss of the percentage of alcohol over time. Spectroscopic methods are currently used with great success in the preparation and testing of pharmaceuticals, the determination of the content of the main components of food (water, protein, lipids, and carbohydrates), as well as in other fields.

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Structure of helminth fauna in *Apodemus uralensis* (Pallas, 1771) from natural and anthropized ecosystems of the Republic of Moldova

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Abstract. The taxonomic structure consists of 3 classes, 10 families, 12 genera and 13 species, of which 6 parasitic species belong to the Cestoda class (*Skrjabinotaenia lobata*, *Catenotaenia cricetorum*, *Hydatigera taeniaeformis*, *Hydatigera taeniaeformis*, *Taenia pisiformis*, *Paranoplocephala omphaloides*, *Rodentolepis straminea*), with a share of 46.1% of the total species, 5 species - to the Secernentea class (*Syphacia obvelata*, *Syphacia stroma*, *Heligmosomoides polygyrus*, *Mastophorus muris*, *Strongyloides ratti*) with a share of 38.5%, and 2 species – to the Adenophorea class (*Trichuris muris*, *Capillaria hepatica*), constituting 15.4% of the total identified species.
Keywords: parasite fauna, *Apodemus uralensis*, biotopes, Republic of Moldova.

Structura helmintofaunei la *Apodemus uralensis* (Pallas, 1771) din ecosisteme naturale şi antropizate ale Republicii Moldova

Rezumat. Structura taxonomică este constituită din 3 clase, 10 familii, 12 genuri şi 13 specii, dintre care 6 specii parazitare sunt din clasa Cestoda (*Skrjabinotaenia lobata*, *Catenotaenia cricetorum*, *Hydatigera taeniaeformis*, *Hydatigera taeniaeformis*, *Taenia pisiformis*, *Paranoplocephala omphaloides*, *Rodentolepis straminea*), care constituie 46,1% din totalul de specii identificate, 5 specii – din clasa Secernentea (*Syphacia obvelata*, *Syphacia stroma*, *Heligmosomoides polygyrus*, *Mastophorus muris*, *Strongyloides ratti*) cu o pondere de 38,5% şi 2 specii – din clasa Adenophorea (*Trichuris muris*, *Capillaria hepatica*), alcătuind 15,4% din totalul de specii identificate.
Cuvinte cheie: parazitofauna, *Apodemus uralensis*, biotopuri, Republica Moldova.

1. Introduction

Small rodents occupy the dominant place among mammals, and from an ecological point of view they are one of the main components of the ecosystem. This group of animals has a beneficial effect on the structure of the soil and the layer of vegetation with grass and shrubs, also representing the main prey of many species of reptiles, prey birds and predatory mammals [10]. In addition to the beneficial effects on the environment,

rodents also have a negative role by being hosts (intermediate, definitive) for a variety of invasive forms of parasitic species characteristic to other animals and humans [1, 2, 3, 4, 6, 8, 17, 18, 28,].

The pygmy field mouse (*Apodemus uralensis*, Pallas, 1771) inhabits the forest edge and open type biotopes: meadows, grasslands, agrocenoses, fallow ground. It is a species of lower frequency and ecological significance compared to other small rodents [10, 11].

Parasitic organisms are an integral part of natural biocenoses. They are of particular importance in the biosphere, through direct involvement in the formation and regulation of biodiversity [5, 13]. Helminths, by interacting with different groups of animals through various ecological connections, form parasite-host systems with increased bioecological stability and represent models for studying the diversity and variability of parasite-host biosystems [23]. Quantitative and qualitative changes of parasite species, age and seasonal infection rates of hosts, characterize the specific changes of certain ecoparasitological situations in different types of ecosystems [7, 13, 14, 15].

The helminthological studies in rodents are of particular interest, because the global and local anthropogenic transformations have a considerable impact on the biodiversity of natural and anthropized ecosystems [21, 22].

The aim of the paper was the ecoparasitological study in order to establish the structure of the parasitic fauna of the host species *Apodemus uralensis* (Pallas, 1771) from different biotopes of the Republic of Moldova.

2. Materials and methods

The small rodents were collected during 2015–2020 years, from different natural and anthropogenic ecosystems of the Republic of Moldova. The capture of the specimens was carried out by placing 100 live traps at a distance of 5 m from each other. This methodology is recommended for biotopes with a well-developed shrub layer and abundant grass cover [12].

The investigations were carried out in the laboratory of Parasitology and Helminthology of the Institute of Zoology, on 20 specimens of *A. uralensis* (5 – ♂, 15 – ♀) collected from various biotopes of the Republic of Moldova. Laboratory parasitological investigations were performed by total dissection of previously euthanized rodents, with microscopic examination of the muscles (masseter muscles, arms, diaphragm) and internal organs (trachea, lungs, heart, tongue, esophagus, stomach, small intestine, large intestine, liver, spleen, kidneys, urinary bladder) in order to establish the structure of the helminth fauna and determine the parasitological indices [20, 25]. The identification of helminth species was carried out on morphological criteria according to standard methods [26, 27].

3. Results and discussions

The pygmy field mouse (*A. uralensis*) was identified on the territory of Moldova in the 80s of the 20th century from the polytypic species *A. sylvaticus* (Linnaeus, 1758). It is slightly larger than the house mouse (*Mus musculus*, Linnaeus, 1758) and smaller than the wood mouse [24]. *A. uralensis* usually prefers different natural (grasslands, forest shelter belts, perennial grass) and artificial (agrocenoses with cereal grasses, annual and perennial agricultural crops) biotopes. It avoids forests, wet meadows and wetlands. It is more frequently found in unprocessed biotopes, such as pastures, landslides with shrubs, thickets. Other types of biotopes are unevenly populated during the year. In autumn and winter, it usually inhabits the forest belts, in summer it can be met in wheat fields, perennial crops – vineyards, orchards. The animal has a predominantly nocturnal activity, it moves at different hours of the night, but sometimes also during the day. They can migrate to neighboring stations at a distance of several hundreds of meters. They live in underground galleries and feed on the seeds of spontaneous plants and agricultural crops, sometimes they consume insects, fruits, berries [9, 10, 16].

The ecological study regarding the preferences and distribution in various biotopes of the host *A. uralensis* compared to other species of small rodents, confirms the character of a spread throughout the whole territory between the Prut and the Dniester rivers. Thus, the higher biotope preference was found in weeding crops with a frequency of 52.6%, followed by unprocessed lands and autumn cereal grasses with 44.3% for each, then forest belts with 34.8%, perennial forage crops – 26.1% and perennial plantations – 17.3%.

The results of the parasitological investigations (tab. 1) carried out on the investigated host species (*A. uralensis*), show a prevalence with *Paranoplocephala omphaloides* of 10.0%, and the mean intensityis of 1.5 sp., respectively with *Rodentolipis straminea* – 5.0%, 2.0 sp., *Hydatigera taeniaeformis* – 10.0%, 1.0, *Catenotaenia cricetorum* – 5.0%,2.0, *Skrjabinotaenia lobata* – 10.0%, 1.5, *Taenia pisiformis* – 10.0%, 1.5, *Capillaria hepatica* – 15.0%, intensitate mică (+), *Syphacia stroma* – 5.0%, 82.0, *Syphacia obvelata* – 20.0%, 83.5, *Heligmosomoides polygirus* – 5.0%, 9.0, *Strongyloides ratti* – 15.0%, 19.7, *Mastophorus muris* – 20.0%, 5.0, and with *Trichocephalus muris* – 15.0%,2.3. Thus, from the total (20 specimens) of hosts examined, 70.0% (14 sp.) were infested with an average intensity of 37.6 specimen/animal.

The highest degree of spread was found with parasitic species *R. straminea*, *S. obvelata*, *M. muris*, *C. hepatica*, *S. lobata* (19.3 – 22.3%), a level of frequent spread was identified in *H. taeniaeformis*, *P. omphaloides*, *S. ratti*, *T. muris* (12,9 – 16,1%), a level of relative

Table 1. Structure of parasite fauna in *Apodemus uralensis* (Pallas, 1771)

Class	Family	Species	Prevalence, %	Intensity, sp.
Cestoda (6 species)	*Catenotaeniidae*	*Skrjabinotaenia lobata* (Baer, 1925)	10.0	1.5
		Catenotaenia cricetorum (Kirshenblatt, 1949)	5.0	2.0
	Taeniidae	*Hydatigera taeniaeformis* (Batsch, 1786)	10.0	1.0
	Mesocestoididae	*Taenia pisiformis* (Bloch, 1780)	10.0	1.5
	Anoplocephalidae	*Paranoplocephala omphaloides* (Herman, 1783)	10.0	1.5
	Hymenolepididae	*Rodentolepis straminea* (Goeze, 1782)	5.0	2.0
Secernentea (5 species)	*Oxyuridae*	*Syphacia obvelata* (Rudolphi, 1802)	20.0	83.5
		Syphacia stroma (Linstow, 1884)	5.0	82.0
	Heligmosomidae	*Heligmosomoides polygyrus* (Dujardin, 1845)	5.0	9.0
	Spirocercidae	*Mastophorus muris* (Gmelin, 1790)	20.0	5.0
	Strongyloididae	*Strongyloides ratti* (Sandground, 1925)	15.0	19.7
Adenophorea (2 species)	*Trichuridae*	*Trichuris muris* (Scrank, 1788)	15.0	2.3
	Capilariidae	*Capillaria hepatica* (Bancroft, 1893)	15.0	+

spread was identified *T. pisiformis* (10,0 %), and in species *S. stroma*, *H. polygyrus*, *C. cricetorum* a rarer spread has been recorded (5,0 – 6,5%).

The highest level of invasion intensity was found with *S. stroma* and *S. obvelata* (83,5 – 82,0 sp./animal), medium level – in *S. ratti* (19,7 sp./animal), and inferior level – in *S. lobata*, *C. cricetorum*, *H. taeniaeformis*, *Taenia pisiformis*, *P. omphaloides*, *R. straminea*, *T. muris*, *M. muris*, *H. polygirus* (1,0 – 2,3 sp./animal).

The taxonomic structure (tab. 1) is divided into 3 classes, 10 families, 12 genera and 13 species, of which 6 parasitic species belong to the Cestoda class, with a share of 46.1%

of the total species, 5 species - to Secernentea class with a share of 38.5%, and 2 species – to Adenophorea class constituting 15.4% of the total species identified.

The evolutionary characteristic (tab. 2) is represented by 6 species that develop according to the monoxenous model (*S. stroma*, *S. obvelata*, *C. hepatica*, *T. muris*, *H. polygirus*, *S. ratti*) and 7 species with polyxenous evolution, including 6 species with development according to the dixenous model with the presence of exogenous forms (*H. taeniaeformis*, *T. pisiformis M. muris*, *S. lobata*, *C. cricetorum*, *P. omphaloides*, *R. straminea*).

Table 2. Evolutive characteristics of the parasites

Model	Class			Total
	Cestoda	Secernentea	Adenophorea	
Monoxenous	-	S. obvelata S. stroma S. ratti H. polygirus	C. hepatica T. muris	6 species
Dixenous	H.taeniaeformis T. pisiformis S. lobata C. cricetorum P. omphaloides R. straminea	M. muris	-	7 species

Analyzing the bioevolutionary characteristic of the parasitic species of the class Cestoda, we find that endoparasitism is represented by 3 species with obligate stationary larval parasitism (*H. taeniaeformis* , *T. pisiformis*) and 3 species (*C. cricetorum*, *P. omphaloides*, *R. straminea, S. lobata*) with imaginal stationary obligate parasitism. While most species of nematodes are geohelminths (*H. polygyrus*, *M. muris*, *S. stercoralis*, *S. ratti*, *A. caninum*, *T. canis*, *T. leonina*, *T. vulpis*, *T. muris*, *C. hepaticum*), which develops freely without intermediate hosts. In the respective species, the embryogenesis and postembryonic evolution take place in the environment, where the free invasive forms keep the infesting property for a long period of time. Some species are geohelminths (*Syphacia stroma, S. obvelata*), they are located in the small and large intestine of rodents and humans, and females can lay fertilized eggs in the perianal region of the host, omitting the stage of development in the environment. Infestation takes place by autoinvasion, individual contact between hosts or by trophic way in carnivores.

Previously, on the territory of the Republic of Moldova, parasitological research was carried out between the 1960s and 1970s, and during this period the species *A. uralensis* was considered *A. sylvaticus*. Later, thanks to research in the field, *A. uralensis* was confirmed as a separate species [24]. Therefore, parasitological investigations from that period in *A. sylvaticus* highlighted an infestation with *Catenotaenia pusilla* – 3,74%, respectively, with *Skrjabinotaenia lobata* – 2,67%, *Rodentolepis straminea* – 3,03%, *Paruterina candeabraria* – 0,72%, *Taenia hydatigena – 0,54%, Hydatigera taeniaeformis* – 1,62%, *Trichinela spiralis* – 1,08%, *Trichocephalus muris* – 1,62%, *Heligmosomum aberrans* – 20,3%, *H. azerbaidjani* – 52,9%, *H. polygyrum* – 11,37%, *H. skrjabini* – 1,6%, *Aspiculurus dinniki* – 0,54%, *A. tetraptera* – 3,74% and *Syphacia stroma* – 8,02% [19].

The parasitological research carried out on samples of *A. uralensis*(*Sylvaemus uralensis*) collected from the National Park "Samarskaya luka" located in the Samara Region, Russian Federation, revealed 19 species of parasites belonging to different taxa: Trematoda - 3 species (*Plagiorchis elegans*, *Dicrocoelium lanceatum*, *Corrigia vitta*), Cestoda – 7 (*Aprostatandrya macrocephala*, *Skrjabinotaenia lobata*, *Catenotaenia cricetorum*, *Hymenolepis diminuta*, *Taenia hydatigena*, *Cladotaenia globifera* , *Hydatigera taeniaeformis*), Nematoda – 8 (*Heligmosomum mixtum*, *Heligmosomoides polygyrus*, Trichocephalus muris, *Syphacia montana*, *S. obvelata*, *Gongylonema neoplasticum*, *Rictularia proni*, *Capillaria annulosa*), Acanthocephala – 1 species (*Moniliformis moniliformis*). Among them, 6 species have a zoonotic and epizootic impact: the trematodes *Dicrocoelium lanceatum*, cestode *Hymenolepis diminuta, Rodentolepis straminea, Hydatigera taeniaeformis* larvae, *Taenia hydatigena larvae* and the nematode *Syphacia obvelata* [21, 22]. A similar study carried out in the Voronezh Region, Russia, shows that the helminth fauna of *A. uralensis* consists of *Syphacia stroma*with a prevalenceof 42,4%, *Syphacia obvelata* – 30,6%, *Heligmosomoides polygyrus* – 29,3% *Syphacia obvelata* – 15,7%, *Heligmosomoides polygyrus* – 25,2%, *Capillaria hepatica* – 8,2%, *Pseudocatenotaenia matovi* – 2,4%, *Trichocephalus muris* – 0,82%, *Ganguloterakis spumosa*–2,3%, *Rictularia proni* – 2,0%, *Mesocestoides lineatus* – 1,2%, *Skrjabinotaenia lobata* – 1,2%, *Plagiorchis elegans* – 1,2%, *Aspiculus tetraptera* – 1,2%, *Alaria alata* – 1,2%, *Hydatigera taeniaeformis* – 0,75%, *Hymenolepis diminuta*–0,42%, *Trichinela nativa* – 0,26% [25].

In this context, the parasitic organisms are an integral part of natural biocenoses, having a particular importance in the biosphere through direct impact on natural biodiversity. This is explained by the fact that helminths interacting with different groups of animals through various ecological connections, form host-parasite systems with increased bioecological

stability, and finally are considered factors regulating the diversity and variability of natural and anthropogenic ecosystems.

4. Conclusions

(1) The taxonomic structure of helminths is divided into 3 classes, 10 families, 12 genera and 13 species, of which 6 parasitic species belong to the class Cestoda (*Skrjabinotaenia lobata*, *Catenotaenia cricetorum*, *Hydatigera taeniaeformis*, *Hydatigera taeniaeformis*, *Taenia pisiformis*, *Paranoplocephala omphaloides*, *Rodentolepis straminea*), with a share of 46,1% from the total species, 5 species – to class Secernentea (*Syphacia obvelata*, *Syphacia stroma*, *Heligmosomoides polygyrus*, *Mastophorus muris*, *Strongyloides ratti*) with a share of 38,5%, and 2 species – to class Adenophorea (*Trichuris muris*, *Capillaria hepatica*) constituting 15,4% from the total species identified.

(2) Parasitological research on the host species *Apodemus uralensis* (Pallas, 1771) highlighted a prevalence with *Paranoplocephala omphaloides* de 10,0%, respectively, with*Rodentolipis straminea* – 5,0%, *Hydatigera taeniaeformis* – 10,0%, *Catenotaenia cricetorum* – 5,0%, *Skrjabinotaenia lobata* – 10,0%, *Taenia pisiformis* – 10,0%, *Capillaria hepatica* – 15,0%, low intensity (+), *Syphacia stroma* – 5,0%, *Syphacia obvelata* – 20,0%, *Heligmosomoides polygirus* – 5,0%, *Strongyloides ratti* – 15,0%, *Mastophorus muris* – 20,0%, and with *Trichocephalus muris* – 15,0%.

(3) The evolutionary characteristic of the helminth fauna is represented by 6 species that develop according to the monoxenous model (*S. stroma*, *S. obvelata*, *C. hepatica*, *T. muris*, *H. polygirus*, *S. ratti*) and 7 species with polyxenous development, including 6 species with development according to the dixenous model with the presence of exogenous forms (*H. taeniaeformis*, *T. pisiformis*, *M. muris*, *S. lobata*, *C. cricetorum*, *P. omphaloides*, *R. straminea*).

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The influence of environmental factors on caudate amphibians at the national, regional and european level: synthetic eco-evolutionary analysis

Tudor Cozari

Abstract. Based on the data obtained in the field and those selected from the specialized literature, there was carried out a synthetic eco-evolutionary analysis of the biology, ecology and ethology of the populations of caudate amphibians at the national, regional and European level. The data obtained can serve as a support scientific-methodological for the evaluation of the ecological status of the populations of caudate amphibians and their conservation.

Keywords: caudata amphibians, polyfactorial analysis, anthropogenic factors, ecological status, amphibian conservation.

Influența factorilor de mediu la amfibienii caudaţi la nivel național, regional și european: analiză sintetică eco-evolutivă

Rezumat. Pe baza datelor obținute în domeniu și a celor selectate din literatura de specialitate, a fost realizată o analiză sintetică eco-evoluționară a biologiei, ecologiei și etologiei populațiilor de amfibieni caudați la nivel național, regional și european. Datele obţinute pot servi drept suport ştiinţifico-metodologic pentru evaluarea stării ecologice a populaţiilor de amfibieni caudaţi şi conservarea acestora.

Cuvinte cheie: amfibieni caudaţi, analiza polifactorială, factori antropici, starea ecologică, conservarea amfibienilor.

1. Introduction

One of the primordial imperatives of contemporary society consists in the protection of the biodiversity of the ecosystems on Earth [4, 9]. However, the well-being of human communities, whether at the local, regional or global level, depends entirely on its beneficial ecological condition. This requires us to take urgent measures to investigate the intra- and inter-population mechanisms of the adaptation and perpetuation of amphibians, which constitute one of the indispensable and important components of the biodiversity of natural ecosystems. In the animal world, amphibians represent one of the indispensable components of ecosystems, they populate the most diverse natural and anthropogenic

terrestrial and/or aquatic habitats. By virtue of the amphibious way of life, this group of animals evaluates as consumers of the first, second and third degrees in the trophic networks of aquatic and terrestrial ecosystems, achieving a continuous and efficient exchange of matter and energy and contributing to maintaining the ecological balance of these natural ecological systems. Regrettably, out of the 3 thousand species of amphibians currently existing on the globe, about 60 species (2%) are threatened with extinction, and 2 species (0.1%) disappeared after the year 1600. It is not known accuracy the number of amphibian species that are today on the verge of extinction, but one thing is certain: in a number of countries of the world, dozens of the representatives of the batrachofauna are assigned to the last category of vulnerability - that of critically endangered species, i.e. those which present an extremely high risk of extinction. The main causes of the deplorable ecological situation in which many species of amphibians have found themselves consist, first of all, in the destruction of habitats and/or in the overexploitation of certain species; most frequently, however, the threat to amphibian species is represented by a complex of causes. And these, to the regret of the specialists in the field, are not always fully known, and sometimes they cannot even be established so easily [1,3].

2. Materials and methods

Following theoretical and practical investigations, there were collected materials regarding the spatial and temporal distribution of more than 25 populations of caudate amphibians within the species' range, both at the local and national, as well as the regional and European level. The data were collected from different aquatic and terrestrial ecosystems during the years 2016-2022. Limiting ecological and anthropogenic factors, acting in particular on population structure, biology, ecology and ethology of caudate amphibians, were assessed. As a result, there was established the current ecological status of the amphibian populations and there were proposed the necessary measures for their conservation in the short and medium term. The need for such research is more than timely, given the fact that only after the elaboration of an integral conceptual framework about the biological and ecological-ethological peculiarities of the populations throughout the entire annual life cycle is possible to evaluate the real ecological state of the amphibian species and to elaborate adequate and effective measures for their monitoring and conservation [2].

3. Results and discussions

The amphibian fauna of the Republic of Moldova, in its current configuration, is partly the result of historical or recent transformations of anthropic origin. Along with indirect

actions, conditioned by essential and unpredictable environmental changes, the negative anthropogenic impact exerted consciously or unconsciously had adverse repercussions on the specific diversity and effective populations. As a result, most of the species of the national batracofauna (except, perhaps, only the green ranid species in some habitats) in the last 20 years have drastically reduced their distribution area and population numbers in most of the natural habitats and, more chosen, in the strongly anthropized ones, the causes of this deplorable ecological situation being multiple. Among them we mention: the fragmentation of natural habitats, which resulted in the disruption of amphibian access routes between the terrestrial nutrition and wintering stations and the aquatic stations used for reproduction; compromising the nutritional base of amphibians in natural habitats due to the degradation of their biodiversity; the clearing of small river meadows, which caused the disappearance of temporary water pools used as breeding stations for amphibians; pollution or destruction of breeding stations, etc. A series of anthropogenic factors act on the spatial distribution, the population numbers and the general ecological state of the caudates within the area, the degree of influence and negative impact of which varies greatly from one region to another. Through long-term special researches, carried out in various European countries [6,7], it has been demonstrated that one of the strong factors of the decrease in the population of paedomorphic newts, along with the fragmentation of natural habitats, is the introduction of the species into water basins fish predators. The investigations carried out demonstrated that, according to the degree of adaptation to different living conditions of the environment, the caudate species are divided into the following three ecological groups: a) forest species; b) species of open habitats; c) amphibian species (with wide ecological plasticity). The distribution of species with wide ecological plasticity (potential) is in full agreement with the density of the lakes, their degree of insolation during the amphibian reproduction period and the presence of other syntopic amphibian species. The species of the genus Triturus, in certain periods of the year, use different habitats - forest and meadow; thus, after leaving the breeding ponds, the newts stay in the meadow habitats for more than a month. In spring and in the first half of summer, the individuals of these populations are in water basins, being active both during the day and at night; then, they go out on land, where they are already active only at dusk and at night. During the day on land they are only encountered in rainy weather or during breeding migrations. The given species, as characteristic habitats, use open grassy, rocky ones, burrows of other animals, etc., males prefer open habitats, and females prefer burrows (due to viviparity).

Through the method of polyfactorial analysis, there were evaluated the ecological factors that influence the spread of species. It has been established that caudate species

prefer lakes that are, at least partially, overgrown with bushes; that is, the population of certain lakes by this species depends on the quality of adjacent terrestrial habitats, where the common newt can live in terrestrial conditions after breeding. It has been found that species of the Triturus genus make extensive use of natural burrows to hide from predators and adverse environmental factors [5]. Females preferentially enter those burrows where males are already present, while for males the presence of females or other individuals in such burrows is of no importance. The problem with the use of temporary water pools by amphibians is that these pools, although they are favorable for the development of larvae, are also unstable as a hydrological regime: when they dry up, these pools lead to the death of larval populations. Thus, some caudates live, as a rule, in the aquatic habitats (78% of the individuals of the population) and only a part of them (22%) – on the moist terrestrial sectors around the aquatic habitats. Following the investigations, it was established that one of the determining factors of the spread of caudates is the presence and distribution of water bodies, which can ensure their successful reproduction [3,6,8]. One of the indispensable ecological parameters of the use of water basins as a place for reproduction is the presence of submerged aquatic plants. It has been established that the water basins where newts reproduce are rich in such vegetation, from which it follows that newts, in this sense, could serve as suitable biological indicators of a rich diversity of vegetation in them. All the amphibians found on the territory of our country hibernate; they appear in early spring immediately after the melting of snow and ice in the water bodies, the date of their appearance and the entire seasonal cycle of reproduction varies according to temperature [1,4,6]. The alternation of aquatic and terrestrial life phases is a typical phenomenon for salamander species [2,9]. It was found that the seasonal movements of the studied caudate and ecaudate species from lakes to terrestrial habitats and vice versa do not occur randomly: the amphibians use certain ”habitat corridors” for this. In relation to this particularity of migration, it is proposed that in cases where it is necessary to create so-called ”buffer zones” around the reproduction pools of the species, the specificity of the spatial location and the configuration of the ”corridors” should be taken into consideration habitats” of amphibian species in these habitats. Following the study of the migration capacity of salamanders, it was established that in 48 hours they can cover a distance of up to 200 m [7].

Another important aspect of the ecology of caudates is related to their ability to recognize (based on certain sense organs) and to return to their native terrestrial habitats after the end of the reproduction process that takes place in water basins. It has been established that caudates have a well-developed so-called ”sense of home” (”homing” - from English), which allows them to safely return to their native habitat after being

transferred to a distance of 213–230 m by this one. Their safe orientation towards their native place of living is due to the previous experience accumulated during the pre-reproductive and post-reproductive migrations, during which the individuals know and memorize the natural terrestrial habitats that are within 230 m of the breeding pool. In sympatric populations of newts, heterospecific crossings are not possible due to the existence of different, species-specific acts of nuptial demonstration. Thus, during homospecific crosses spermatophore transmission occurs in 34 percent of cases, while after heterospecific crosses - only in 4 percent of cases.

Chemoreception plays a primary role in achieving orientation and locomotor behavior by caudate amphibians. Following some special studies, it was found that in the species of the Salamandridae family, for example, while searching for burrows, individuals orient themselves by the smell emanating from other individuals, this allowing them to populate the same burrows with several individuals of the same species [1,6]. It is assumed that this tendency of individuals to aggregate presents an adaptation for survival in dry habitats, because, gathering several together in the same burrows, the integument of individuals resists drying much more easily. The diurnal activity of salamanders changes when the presence of predators is signaled, it obviously decreases [6].

It has been established that chemoreception plays an important role in newt communication [8]. Thus, in the Triturus helveticus species, the odors of conspecific individuals facilitate the process of association and formation of nuptial groups in the breeding pools. In the species Salamandra desmognatus ochrophaeus, the phenomenon of recognizing conspecific individuals based on the olfactory markings left on the substrate by different individuals was established: young males avoided the smell of mature males (to avoid cannibalism) [2, 4]. Depending on the degree of evolution of different species of salamanders, the process of chemical communication between conjugal partners is carried out differently [1, 8]. In the species of the most primitive group of the genus Plethodon - the ”cinereus” group, the males, in order to transmit the sexual pheromones, use the ”vaccination” procedure: strongly rubbing the skin of the females with the help of special premaxillary teeth, they then introduce this place the sexual pheromones that are produced by the submaxillary glands. The second group of species - ”gluinobius”, being more evolved, carries out the transmission of male sexual pheromones directly from the sexual glands to the nostrils of the females. However, there are also species, such as Plethodon dorsales, which occupy an intermediate position in terms of sexual behavior compared to the two groups of salamanders mentioned previously.

In laboratory conditions, the males of some species of caudates, such as those of Plethodon vehiculum and P. dunni, can determine by smell the chemical messengers

emitted by mature and young females [7]. While the females, unlike the males, were not able to distinguish the young males based on the sexual pheromones eliminated by them. In this way, it was demonstrated that males are able to choose females ready for reproduction, while females - only the largest males. Often, in order to successfully carry out some investigations related to the nuptial behavior of newts, along with the classical methods, it is also necessary to develop some original research methods. Thus, one of the effective methods of studying the behavior of caudate and ecaudate amphibians, along with photographing demonstration pictures of males and females, is the representation of these behavioral acts through schematic drawings. Schematic drawings have priority in that they allow highlighting and representing only those particularities of animal behavior that represent the ”quintessence” or ”key-particularity” of one or another behavioral act. In this way, the researcher has the opportunity to accumulate, systematize, analyze and expose these behavioral acts in a certain consecutiveness and interconnection that other illustrative research methods cannot provide. In many works, certain aspects of the territorial behavior of some species of Salamandridae, such as Eurycea wilderae, are analyzed [2,4]. In the territorial behavior of salamanders, which is quite original, certain specific behavioral acts are attested, such as ”aggression behavior” towards intruding individuals. It was found that the resistant individual, being disturbed, always shows an aggressive behavior, while the intruder avoids direct confrontations with him, regardless of his body size or previous experience of such confrontations. These behaviors once more prove to us that salamanders are strictly territorial animals during the breeding season. They show territorial antagonism not only towards related species, but even towards other foreign syntopic species of hydrobionts. In addition to the fact that both the forest salamander (Plethodon cinereus) and the centipede Scolopocryptos sexspinosus use similar hiding places (galleries under stones on the bottom of the water), these species show a negative spatial correlation. So, for example, only in 7 hiding places out of the 247 examined, under some and the same stones were both species. This is due to the fact that the salamander attacks this millipede and drives it out of its favorite hiding places [1,3]. Following some research, carried out both in laboratory conditions and in natural conditions, it was established that the nuptial behavior of different species, as expected, differs more obviously than in the cases of nuptial behaviors manifested by the subspecies of the same species [4 ,6,8]. Precisely because of this, subspecies hybridize much more frequently in nature than sympatric species. In the sympatric populations of T. vulgaris and T. montadoni, heterospecific crossings are not possible due to the existence of different, species-specific acts of nuptial demonstration [5,7]. Thus, during

homospecific crosses spermatophore transmission occurs in 34 percent of cases, while after heterospecific crosses - only in 4 percent of cases.

It is known that the reproductive behavior of caudate amphibians is stereotypical, from which it can be hypothesized that it is genetically coordinated. Following special research on the subject, it was established that the consecutiveness of the manifestation of certain behavioral acts by the partners during the nuptial games is not strictly regulated from a genetic point of view, this giving the species the opportunity to manifest a certain behavioral plasticity, which, in his opinion, has a certain adaptive importance in the conditions of unpredictable fluctuations of the environment. In the populations of Triturus vulgaris that are in unfavorable conditions of existence, the oviposition process of the females is directed towards the economy of the available vital energy. For this reason, females become fertile at a smaller body size than females in populations with optimal living conditions, lay smaller eggs and, at the same time, end their breeding season much earlier than in optimal living conditions. The survival strategies of the larvae depend on the altitudinal distribution of the biotopes; being strongly influenced by temperature, certain adaptations to these environmental conditions appear in larval populations. The larvae are resistant to frost for a short period of time and this resistance depends on the thermal capacity of the brood. Larvae in temporary pools, which have high water temperature but dry up every year, develop very quickly. In medium-sized pools, rich in vegetation, larval development, on the contrary, proceeds at a normal rate. The rate of larval development of newts also depends on the influence of the metabolites eliminated by the larvae of other syntopic caudate species. It has been established that in different breeding pools the size of the larvae depends on their density: in conditions with a high density, the larvae are small, while in populations with a low density the larvae are larger. When there are several generations of larvae in aquatic pools, the larger generations influence the smaller ones through cannibalism, the phenomenon in question being due to the different sizes of the larvae. There is the so-called priority effect: priority is given to larger larvae and then density regulation takes place to exclude cannibalism and intraspecific competition. As a result of the investigations, it was demonstrated that cannibalism is an effective mechanism for regulating the density of larval populations only in highly variable environmental conditions. The cannibals, consuming a large number of conspecific larvae, contribute, in this way, to the decrease of the density; and, on the other hand, they contribute, at the same time, to the intensification of the process of the individual development of the larvae and, as a result, to their earlier emergence on land.

Anthropogenic factors have a particular influence on the spread and reduction of amphibian populations. One of the anthropogenic factors with a strong negative action that

leads to the extinction of caudate species is deforestation; phenomenon reported in forest ecosystems: in all sectors cut from the forest, the density and diversity of salamanders has decreased a lot. Also, in a number of areas of Europe, the caudates, due to the destruction of their habitats, are disappearing, being ranked in the category of endangered species. Due to the damming works and the acquisition of gravel, various species of the genus Triturus have disappeared in a number of habitats of our country. Roads also have a negative impact on amphibians because they lead to the fragmentation of populations, preventing their free movement in the given natural habitat. During migrations, due to roads, up to 51% of individuals do not return to their natural habitat. One of the causes of the disappearance of the species Triturus vulgaris from a series of aquatic habitats is the introduction of predatory fish species. The predatory fish destroy the mature individuals and larvae of Triturus vulgaris, the eggs not being consumed because they are hidden in the leaves. It has been established that one of the causes leading to the demise of certain amphibian populations is the different degree of mortality of mature individuals; where it is higher, the total disappearance of populations is reached, because both in established populations and in those on the verge of extinction, the mortality of larvae and juveniles is approximately the same. In areas strongly affected by anthropogenic factors, some species of amphibians can be successfully used in testing the quality of the environment; first of all, of the degree of pollution of aquatic habitats [4]. In order to protect the caudates, it is proposed to create terrestrial buffer zones (with a width of 50 m on either side of the streams) where the species spend their lives after they have completed their reproduction in the water and have come out on land. The research carried out on this subject has shown that salamanders, once they are on land, do not move away from the water at a distance greater than 43 m. They use these adjacent areas as a characteristic habitat for life, along the streams of the hydrographic networks forming the so-called ”housing corridors”, which ensure the existence of species in the post-reproductive phase of life. Therefore, in order to protect the caudates, we must take under protection these habitat corridors of terrestrial habitats. During the formation of large lakes in spring, which, later, are accompanied by a partial separation following the drying of certain aquatic sectors, it is important to preserve their integrity by digging trenches that would ensure the connection between them to maintain a constant biotope. Some scientists believe that it is very important to study autecology in the development of effective protection methodologies, especially for the populations of little-studied species [3,6,7].

4. Conclusions

The level of research on caudate amphibians, with reference to the number of species examined and the problems addressed, is very different: many of the European caudate species are analyzed from a general point of view, without specifying the entire complex of particularities of their biology, ecology and behavior in the diverse and strongly fluctuating conditions of the environment. And autecological and long-term researches of many species of the genus Trirurus are completely missing. Caudata, as a result of the high degree of primitivism in morphological organization, are subject to much stronger environmental and anthropic influences than the other systematic groups of amphibians. The caudate species, at the same time, also show a certain level of morphological, physiological, ecological and ethological specialization, which, on the one hand, ensures their existence in different environmental conditions of natural habitats, and on the other hand, allows them to colonize to a certain extent and some anthropized habitats; especially those habitats that offer them, first of all, minimal but sufficient conditions for reproduction. The continuation of long-term ecological monitoring research of caudate amphibians is not only timely, but also of particular importance for the sustainable management and protection of their populations. For the successful conservation of caudate amphibians, it is strictly necessary:

a) to protect the natural habitats of the populations and, in particular, of the breeding ones;
b) to avoid the pollution of temporary and permanent stagnant water bodies;
c) to avoid the disturbance of breeders and to preserve amphibian wintering stations;
d) to collect amphibian eggs and larvae from lakes subject to drying or pollution and to transfer them to other water bodies;
e) to avoid the remediation of river meadows in order to preserve aquatic reproduction pools;
f) to provide ecological education for the population, including the young generation, etc.

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The specificities of the thinking process in adolescents. Clip thinking

Diana Koshkodan and Lora Moshanu-Shupac

Abstract. The article describes the so-called clip thinking in adolescents. It has been established that, despite the existing data in the literature on the influence of the Internet on cognitive processes, a decrease in the speed of thought processes in adolescents has not been confirmed. At the same time, there were found a greater number of errors in the reproduction of information in adolescents compared to adults.
Keywords: clip thinking, attention, cognitive processes, adolescents, adults.

Particularităţile procesului de gândire la adolescenți. Gândirea clip

Rezumat. Articolul descrie așa-numita gândire clip la adolescenți. S-a stabilit că, în ciuda datelor existente în literatura de specialitate privind influența Internetului asupra proceselor cognitive, o scădere a vitezei proceselor de gândire la adolescenți nu a fost confirmată. Totodată, s-au constatat un număr mai mare de erori în reproducerea informațiilor în rândul elevilor comparativ cu adulții.
Cuvinte cheie: gândire clip, atenție, procese cognitive, adolescenți, adulți.

1. Introduction

The fast-paced life, the development of advanced technologies and, accordingly, the increase in the flow of information, the need to obtain and process a very large amount of information could not but affect the thinking of our contemporaries. An overloaded brain quickly loses the ability to analyze, choose and decide. This phenomenon especially affects young people, children, who sometimes cannot tear themselves away from the Internet, gadget, phone, etc. [2].

According to Daniel J. Levitin [4], in 2011, Americans were consuming five times as much information per day as they were in 1986—comparable in volume to 174 newspapers. Moreover, 21,274 TV channels produce 85,000 hours of original programming every day, which people watch on average about 5 hours a day, which is equivalent to 20 gigabytes of photo and video information. Every hour, 6,000 hours of video clips are posted on the YouTube channel. And, in total, according to Daniel Levitin, from 2005 to 2015,

mankind created about 300 exabits of information, which corresponds to six trillion War and Peace novels.

The human brain is capable of handling large amounts of information, but its performance comes at a cost. When it comes to separating important data from non-essential data, people face fatigue. Neurons that require oxygen and glucose to function are rapidly depleted.

The term "clip culture" was coined by Alvin Toffler in 1980 in response to a huge amount of information [6, 7, 8]. Clip thinking is a means of obtaining and assimilating information not in the form of a printed text, as people of previous generations used to, but in the form of images, fragments of unrelated facts that follow each other as in a kaleidoscope. While video games can develop visual recognition skills by quickly shifting attention from one image to another, the side effect is automation and reduced correctness of thought processes. The influence of PCs and mobile phones on attention does not disappear when they are turned off, as the cellular structure of the human brain adapts to the tools we use. Irrational clicks on network links, endless flickering of "catchy" headlines, commercials, short, unrelated texts, gadgets with scraps of information - all this makes our consciousness fragmented, cut off. Consequently, wanting to keep up with the fast pace of life, a person ceases to perceive information and receives only superficial facts, [Robert Epstein, 1].

According to the research, people who read information with embedded links understand less than those who read traditional texts [5]. Those who watch a multimedia presentation remember less than those who read information in a book. People who are daily distracted by emails, alerts, messages in programs understand the problem with greater difficulty than those who manage to control them and prioritize them correctly.

Finally, employees who perform many online tasks are less creative and less productive than those who are engaged in one thing that captures their focus entirely.

2. Objectives and methods

The research objectives are determining the speed of the distribution of attention in adolescents and adults; determining the amount of information acquired from the Internet by adolescents and adults.

The studies were carried out at Republican Theoretical Lyceum "Aristotle" (teenagers) and at Tiraspol State University located in Chisinau (master degree students, adults).

(1) Test for determining the level of attention "Prague" (Prague Psychotechnical Institute [3],

(2) Determining the amount of information acquired from the Internet by adolescents and adults. A questionnaire entitled "Diamonds" is proposed with 10 questions on an unknown topic for respondents. Within 7 minutes, the subject must correctly answer the maximum possible number of questions. The answers to the questionnaire can be found in various sources on the Internet.

(3) Statistical data processing was carried out using the SPSS (Statistical Package for the Social Sciences) program.

3. Results and discussions

The data obtained as a result of the Prague test are shown in Fig. 1. Thus, clear differences in the redistribution of attention in people of different ages were revealed.

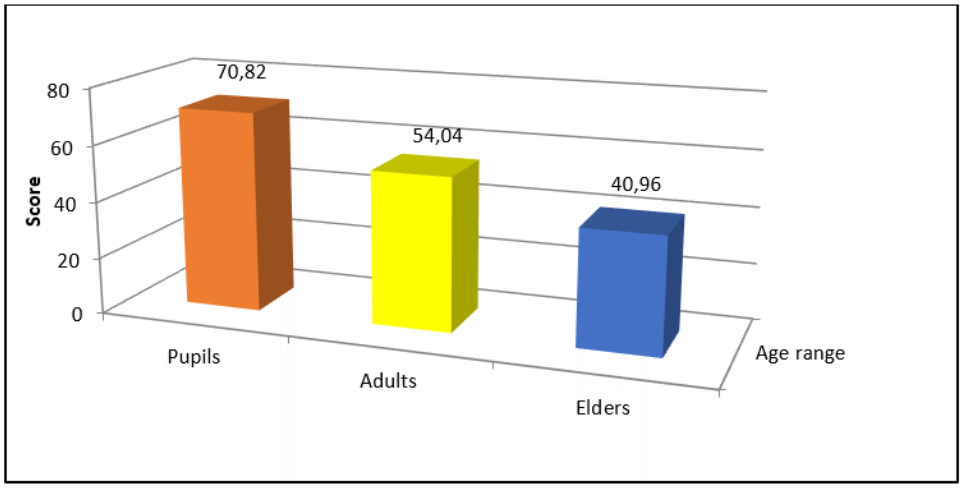

Figure 1. Average score obtained in the Prague Test.

The best result, 70.82 points, was shown by 28 students aged 13-18. The second most important result, 54.04 points, was shown by 25 students aged 38-42. These results revealed significant differences between the student and adult 38-42 sample mean in favor of students, as the mean of this sample is $70.82 > 54.04$ ($p = 0.000 \leq 0.05$).

The third most important result, 39.4 points, was shown by 25 adults aged 65-69 years. These results show significant differences between the averages of the samples of pupils and adults aged 65-69 in favor of pupils, since the average of this sample is $70.82 > 40.96$. ($p = 0.000 \leq 0.05$). To study the speed of cognitive processes, we invited the subjects to study various sources on the topic "Diamonds" on the Internet for 7 minutes, after which

they had to answer the maximum possible number of questions on the topic. The research results are presented in Fig.2.

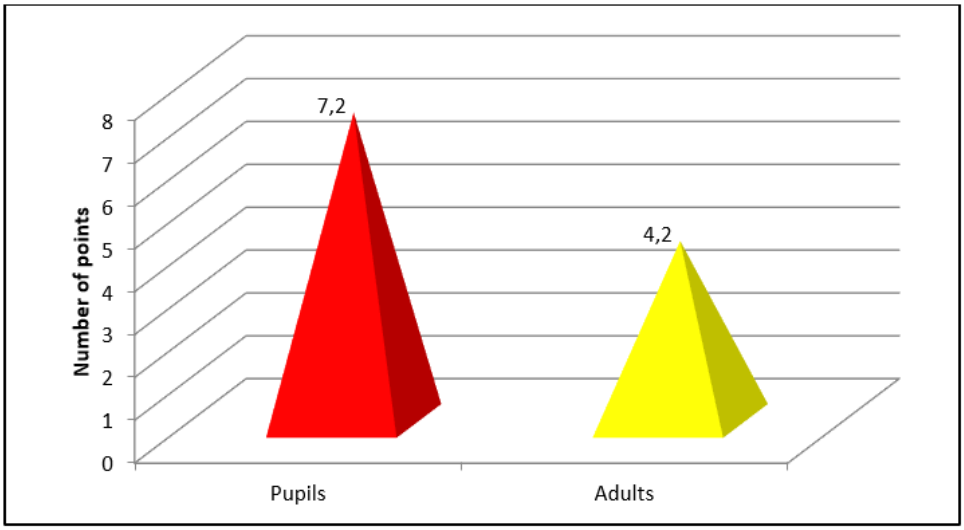

Figure 2. The number of correct answers (in points) for the "Diamonds" test.

Thus, the adolescents showed the greatest number of correct answers - 7.2 points, while the adults scored a significantly smaller number - 2.5 points. These results show significant differences between adolescents and adults sample averages in favour of the adolescents, since the mean of this sample is $7.096 > 4.204$ ($p = 0.000 \leq 0.05$). The original hypothesis was that younger people would score lower than adults or older people as they would be more distracted and find it harder to focus their attention.

Contrary to expectations, the average score of 17-18-year-olds was 7.2, which is much higher than that of 27-51-year-olds, who scored 4.20. More interestingly, among the answers provided, 7.48% were incorrect in the case of young people, and only 4.44% in the case of older people. That is, the latter answered fewer questions, but with somewhat greater accuracy. Thus, this experiment confirmed the presence of accelerated thinking in young people, which, due to the high speed of cognitive processes, makes it possible to cover a wider area of the subject being studied, but has a big drawback – the superficiality of assimilated information.

In general, based on the results of the two experiments, it can be argued that young people did not demonstrate such features of cognitive processes that specialists operate with, such as lack of concentration, short attention span, or superficiality (at least when reading some classical texts). Their flexible thinking is easier to navigate in a large flow of information, given the environment in which they grew up in. However, some aspects

of clip thinking may be present, due to somewhat less accuracy in completing complex and tedious tasks, as in the last experiment, but offset by the greater number of tasks they can perform. This is a useful adaptation in technology and information.

4. Conclusions

(1) The best result in the Prague test was shown by people aged 13-18 - 70.82 points. On the second place, we have the adults with a score of 54.04 points, and on the third place - the elderly participants with a score of 40.96 points.

(2) It was confirmed that young people have accelerated thinking, which, due to the speed of cognitive processes, allows them to cover a wider area of the subject being studied, but has a big drawback - the superficiality of the information being assimilated.

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Aspects on the bird fauna's diversity in the sector Golăieşti - Cotul Bran (Iaşi county, Romania)

Diana-Roxana Tofănescu and Carmen Gache

Abstract. The present study had followed to evaluate the bird fauna's diversity and the seasonal dynamic of birds' population in the sector of Golăieşti – Cotul Bran, related to the common Jijia and Prut Rivers' basin. We did our fieldwork in the years 2014 and 2015. The bird fauna's list includes 117 bird species. The typically woodland bird species are dominant like diversity, but also through their effectives. The wetland bird species present small populations, appearing during the migration time. The breeding bird fauna include 77 certainly breeding species, other 6 species being irregular or probably breeding species in the area. During our study, we identified 21 bird species that appear in the Annex 1 of Birds' Directive, respectively, 12 bird species included in the Romanian Red Book of Vertebrates.
Keywords: bird fauna, habitats, Natura 2000 network, threatening risks.

Aspecte ale diversităţii ornitofaunei în sectorul Golăieşti - Cotul Bran (Iaşi, România)

Rezumat. Studiul nostru a urmărit evaluarea stării actuale a diversităţii, dar şi dinamica sezonieră a ornitofaunei din sectorul Golăieşti – Cotul Bran aparţinând luncii comune a Jijiei şi Prutului. Activitatea de monitorizare a păsărilor s-a desfăşurat în perioada anilor 2014 – 2015, cu deplasări lunare pentru acoperirea tuturor etapelor ciclului biologic anual caracteristic păsărilor. Lista ornitofaunistică este formată din 117 specii de păsări, dominante fiind speciile forestiere atât prin diversitate, cât şi prin efectivele prezente în regiune. Majoritatea speciilor caracteristice ecosistemului acvatic prezintă efective mici, cele mai multe fiind semnalate pe durata migraţiei. Ornitofauna clocitoare este reprezentată prin 77 specii regulat clocitoare, alte 6 specii fiind probabil sau neregulat clocitoare în zona investigată. Pe durata studiului nostru, am identificat 21 de specii de păsări incluse în Anexa 1 a Directive Păsări, respectiv, 12 specii incluse în Cartea Roşie a Vertebratelor din România
Cuvinte cheie: ornitofaună, habitate, rețeaua Natura 2000, factori de risc.

1. Introduction

The location of Golăiești commune (Iași County) is in the area between Romania and the Republic of Moldova, located in the middle sector of Prut River basin. The Jijia

and Prut rivers form a common meadow area there, their valleys presenting a parallel transect and covering a width of 4 – 7 kilometres (km). Regarding geomorphology, the territory belongs to the Moldavian Plateau at the limit between the Moldavia Plain and the Prut Plain. The Jijia River presents a meandering and regularised sector on the territory of commune Golăiești, along 18 km before the confluence point with the Bahlui River. The Prut River represents the eastern limit of the commune along 23 km, presenting large meanders [1]. There was no recorded flooding phenomenon on the territory of the villages crossed by the Jijia River (Cotu lui Ivan, Grădinari, Golăiești and Podu Jijiei) after the hydrotechnic arrangements of Jijia (1985 – 1989) and in the condition of prolonged droughts affecting this region during the last two decades.

The climate is temperate-continental, with hot and dry summers, while the winters are frosty, and it has been poor in snowfalls during the last decade. The average annual temperature is 9.5^o C. The effects of global climate changes are visible in this region. We notice a high amplitude of the thermal variation between summer and winter, while the rainfall regime has become deficient, falling below the multiannual average value of 471.2 mm/annual. The ice-bed covers the river bed for about 90 days.

On the territory of Golăieşti commune, the habitats are characteristic for the dry steppe and forest areas, the cultivated lands and grasslands covering the largest surfaces. On the cultivated lands, we saw cereals, corn and sunflower, other agricultural crops covering small surfaces. The grasslands (*Festuca* sp., *Stipa* sp., *Poa* sp., *Trifolium* sp. etc.) with shrubs and bushes (*Prunus spinosa, Sambucus nigra*, *Cornus mas*, *Rosa canina*, *Rhamnus frangula* etc.) represent the second habitat type as surface in the area. The mixed hardwood forest (*Quercus* sp., *Fraxinus* sp., *Ulmus* sp., *Tilia* sp., *Acer* sp., *Prunus avium*) and acacia plantations (*Robinia pseudacacia*) appear on the slopes from the right side of the Jijia and Prut Rivers valleys. The natural meadow forest (*Populus alba*, *Salix* sp.) is present along the bed of the Prut River, with a well-preserved sector in the perimeter of Cotul Bran, near the village Podu Jijiei [2]. Extensive plantations of Euro-American poplar (*Populus eurocanadensis*) are present on the bank of the Prut River. We found a well-preserved woodland with pedunculated oak (*Quercus robur*) near the village Petreşti-Medeleni, belonging to a private owner that dug a deep ditch around the perimeter of forest. The reed beds cover small areas in the perimeter of Old Jijia (the former natural meanders of river) and some pointed areas along the right bank of the Prut River.

The fauna is relatively poor. The groups of insects present the highest diversity between the invertebrates. The fish fauna of Prut River belongs to the barbel zones (*Barbus barbus, Cyprinus carpio, Abramis brama*, *Tinca tinca*, *Esox lucius*, *Silurus glanis*), while the

Cypriniformes are dominant in the water of the Jijia River (*Cyprinus carpio*, *Carasius gibelio*, *Scardinius erythrophthalmus*, *Alburnus alburnus*, *Misgurnus fossilis*). We notice the presence of amphibians (species complex *Pelophylax kl. esculentus*, *Hyla orientalis,* species complex *Hyla arborea*, *Bombina bombina*, *Pelobates fuscus*, *Bufotes viridis*, *Triturus cristatus*, and *Lissotriton vulgaris*) and some reptile species (*Emys orbicularis*, *Lacerta viridis*, *Lacerta agilis*, *Natrix natrix*, *Natrix tessellata*). The rodents (*Lepus europaeus*, *Spermophillus citellus*, *Cricetus cricetus*, *Nannospalax leucodon*, *Apodemus agrarius* etc.) are the most dominant from the mammal group, but there are other species also present in the area as the ungulates (*Capreolus capreolus*, *Sus scrofa*) and carnivorous (*Vulpes vulpes*, *Lutra lutra*, *Meles meles*, *Mustela putorius*, and *Mustela nivalis*).

It is no previous study regarding the bird fauna from the territory of commune Golăiești. Available old data related to the presence of birds in the perimeter of the Prut and Jijia Rivers appear in the studies done five decades ago [3, 4, 5, 6], as well as results of recent researches following the bird fauna as a whole [7, 8, 9, 10] or some groups of species [11, 12, 13, 14]. Dan Stănescu presented observation on the diversity of birds in the wetlands of the Prut River 55 years ago [15], studying an area located in the southern vicinity of Golăiești commune, in the perimeter of Bosia – Cristești (these wetlands disappeared).

The territory of Golăiești commune overlaps partial or complete with the perimeter of some natural protected areas. The natural protected area IV-2554 Cotul Bran on the Prut River, located near Podu Jijiei village, has protection status on local level from 1994 [16] and on national level from 2000 [17]. This territory is part of two Natura 2000 sites: ROSCI0123 Prut River [18, 19], respectively ROSPA0163 Prut River [20, 21].

The sector Cotul Bran on the Prut River is a meander of the Prut River (Figure 1) and represents a significant reproduction territory for 20 fish species, and shelters also other protected animal species [19].

At the same time, the Valley of the Prut River is part of a significant flyway for the birds' migration in the eastern part of Europe. On the territory of Golăiești commune, the Prut River presents some unfrozen sectors during winter, sheltering population of waterfowls in this part of Romania [9, 10, 20, 21].

2. Period and methods of study

We have done our field study through monthly visits during 2014 – 2015, following the monitoring of bird fauna diversity. We tried to assess the present status of the bird populations and identify the main threatening factors for the bird fauna and biodiversity on the territory of Golăiești commune.

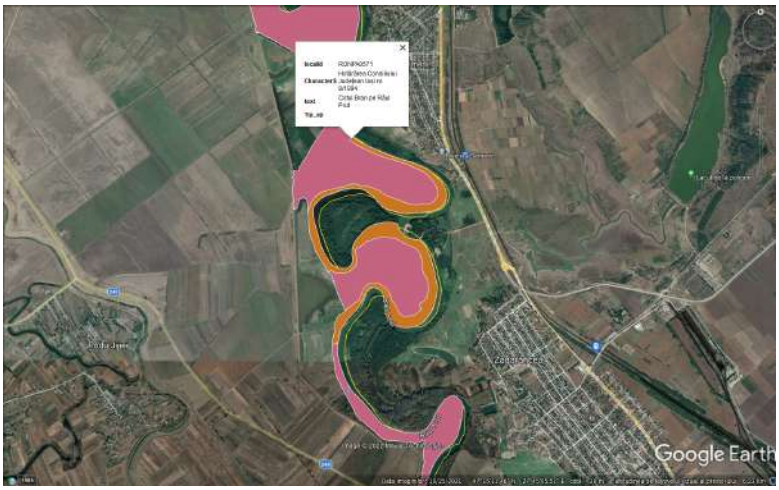

Figure 1. Natural protected area Cotul Bran on the Prut River, part of the Natura 2000 Network in Romania (source: Iași County Environment Protection Agency, Romania)

The monitoring of birds was done using the methods of transect and fixed points, using also the males' calling activity. We established some transects following the communal roads and protective dykes of the two watercourses Jijia and Prut, crossing all types of habitats in the investigated territory. The total length was about 22 km and we used pedestrian walking and a car during our monitoring activity. Stationary in fixed points allowed us to identify and estimate the bird diversity and populations in the area. We used the males' calling activity to identify and estimate the populations of passerines in the reed beds and woodlands, respectively, the hidden life bird species inside compact vegetation, the crepuscular and nocturne ones.

We identify the birds through direct observation by binoculars Pentax 10x42 DCF HRc and telescope HAKUBA 35x70. In the analysis of our results, we are using SIBLEY & AHLQUIST taxonomic system (1995) with subsequent additions and modifications [22, 23].

3. Result and discussions

During our field monitoring activity, we identified 117 bird species, as we present in the table 1. The mentioned values for the bird population represent the minimum, respectively, the maximum number of counted birds or estimated population during one-day visit in the whole territory in the migration and wintering time; we estimated the breeding bird populations using the visual and auditory recordings.

Taxonomical, the passerines (Passeriformes) are dominants, with 72 species, followed by the diurnal raptors – Accipitriformes, with 7 species and the woodpeckers (Piciformes) with 6 species. The other orders have two – five species present in the investigated territory and two orders (Cuculiformes and Bucerotiformes) have one representing species in the area, and in Romania, too.

We recorded the highest diversity of bird fauna inside the ecosystem of forest (68 species) and we met 55 bird species in the perimeter of open areas, covered by grasslands and agricultural lands, with shrubs and bushes, representing the largest habitat in the investigated territory. The low number of the characteristic aquatic and semiaquatic birds (25 species), recorded in the area, reflects the poor quality of typical habitats of wetlands in the study area. Inside the villages we observed 24 bird species.

The breeding bird fauna represent a significant parameter for the assessment of the quality of suitable habitats from one territory because the bird species have strict nesting site requirements. We identified 77 regular breeding bird species, other six species being at least irregular breeding birds in the perimeter of Golăiești commune. On the territory of our country the breeding season of bird species covers a period of seven months, beginning in February for some sedentary species as the corvids (*Corvus corax, Corvus frugilegus*) that start to build or consolidate the nests in the middle February. The other sedentary bird species begin the territorial songs in the late February or early March. Some bird species have fledging chicken from the second, third or even fourth broods in August (for example, *Hirundo rustica, Streptopelia decaocto*).

During the first decade of March, we observed the territorial song activity (delimitation, occupation, marking and defence of breeding territory) of passerine species that build their nests in the open lands as dry grasslands and cultivated lands (*Alauda arvensis* or *Galerida cristata*). Other species as *Anthus campestris*, *Motacilla flava* and *Motacilla alba* arrive during March and in the first part of April, occupying breeding territories and building their nests as large cups woven from grasses among the herbs on the ground, as well as inside the shrubs or tall and thick grasses (for example, *Emberiza calandra*). In the same area we met the wheatear (*Oenanthe oenanthe*).

Starting from April, the warblers (*Curruca curruca* and *Curruca communis*), the shrikes (*Lanius colllurio* and *Lanius minor*), as well as the winchat (*Saxicola rubetra*) and the European stonechat (*Saxicola rubicola*) occupy the shrubs and bushes area, building their nests inside it and using as survey points to search and find the potential preys by flying to the ground and catching it. Most of them have the brood complete in the late April or even in the early May.

Table 1. Bird fauna recorded in the sector Golăiești - Cotul Bran (Iași), during the period 2014 – 2015

No.	Species	Breeding (pairs)	Migration (individuals)	Wintering (individuals)	Suitable habitats				Birds' Directive	Romanian Red Books
					Forest	Wetlands	Open lands	Villages		
1.	*Phasianus colchicus*	8 - 12	x	x	-	-	+	-	A2	-
2.	*Perdix perdix*	7 - 8	x	x	-	-	+	-	A2	-
3.	*Coturnix coturnix*	4 - 5	x	-	-	-	+	-	-	-
4.	*Cygnus olor*	-	1 - 5	2 - 6	-	+	-	-	A2	-
5.	*Anas platyrhynchos*	1 - 2	18 - 58	14 - 72	-	+	-	-	A2	-
6.	*Anas crecca*	-	2 – 10	0 - 4	-	+	-	-	A2	-
7.	*Nycticorax nycticorax*	-	0 – 2	-	-	+	-	-	A1	V
8.	*Ardea alba*	-	0 – 3	-	-	+	-	-	A1	E
9.	*Ardea cinerea*	-	2 - 7	0 - 1	-	+	-	-	-	-
10.	*Platalea leucorodia*	-	0 - 4	-	-	+	-	-	A1	E
11.	*Ciconia ciconia*	4 - 7	35 - 145	-	-	+	+	+	A1	V
12.	*Ciconia nigra*	-	6 - 12	-	-	+	-	-	A1	V
13.	*Buteo buteo*	-	4 - 13	5 - 7	+	-	+	-	-	-
14.	*Buteo lagopus*	-	1 - 5	2 - 4	+	-	+	-	-	-
15.	*Pernis apivorus*	-	3 - 7	-	+	-	+	-	A1	V
16.	*Accipiter gentilis*	-	2 - 4	1 – 2	+	-	+	+	-	-
17.	*Milvus milvus*	-	0 – 1	-	+	-	+	-	A1	V
18.	*Milvus migrans*	-	0 - 2	-	+	-	+	-	A1	CE
19.	*Circus aeruginosus*	0 – 1?	1 – 3	-	+	-	+	-	A1	-
20.	*Falco columbarius*	-	-	1 - 2	+	-	+	-	A1	-
21.	*Falco subbuteo*	1 – 2	3 – 7	-	+	-	+	-	-	-
22.	*Falco tinnunculus*	1 – 2	5 - 7	0 - 1	+	-	+	-	-	-
23.	*Fulica atra*	1 – 2?	6 - 13	-	-	+	-	-	A2	-
24.	*Gallinula chloropus*	2 - 3	4 – 7	-	-	+	-	-	A2	-
25.	*Vanellus vanellus*	-	11 - 17	-	-	+	-	-	A2	-

No.	Species	Breeding (pairs)	Migration (individuals)	Wintering (individuals)	Suitable habitats				Birds' Directive	Romanian Red Books
					Forest	Wetlands	Open lands	Villages		
26.	*Larus cachinnans*	-	2 - 4	-	-	+	-	-	A2	-
27.	*Chroicocephalus ridibundus*	-	4 – 11	-	-	+	-	-	A2	-
28.	*Chlidonias hybrida*	-	2 – 4	-	-	+	-	-	A1	-
29.	*Sterna hirundo*	-	1 – 3	-	-	+	-	-	A1	-
30.	*Columba palumbus*	3 – 5	30 - 42	2 - 4	+	-	-	-	A2	-
31.	*Streptopelia turtur*	9 - 11	7 - 26	-	+	-	+	-	A2	V
32.	*Streptopelia decaocto*	18 - 21	-	22 - 32	-	-	+	+	A2	-
33.	*Cuculus canorus*	5 - 8	x	-	+	+	+	-	-	-
34.	*Athene noctua*	3 - 4	-	x	-	-	+	+	-	-
35.	*Asio otus*	1 – 2	x	x	+	-	-	-	-	-
36.	*Strix aluco*	1 – 2	x	x	+	-	-	-	-	
37.	*Alcedo atthis*	2 - 3	1 - 3	-	-	+	-	-	A1	-
38.	*Merops apiaster*	8 - 12	18 - 34	-	-	-	+	-	-	-
39.	*Upupa epops*	6 - 8	4 - 11	-	+	-	+	-	-	V
40.	*Picus viridis*	2 - 3	x	x	+	-	-	-	-	-
41.	*Dendrocopos major*	7 - 8	x	x	+	-	-	+	-	-
42.	*Dendrocopos syriacus*	5 - 7	x	x	+	-	+	+	A1	-
43.	*Dendrocoptes medius*	1 - 2	x	x	+	-	-	-	A1	
44.	*Dryobates minor*	2 - 3	x	x	+	-	-	-	-	-
45.	*Jynx torquilla*	2 - 4	x	-	+	-	-	-	-	E
46.	*Oriolus oriolus*	9 - 11	x	-	+	-	+	+	-	-

No.	Species	Breeding (pairs)	Migration (individuals)	Wintering (individuals)	Suitable habitats				Birds' Directive	Romanian Red Books
					Forest	Wetlands	Open lands	Villages		
47.	*Lanius collurio*	26 - 28	13 - 21	-	-	-	+	-	A1	-
48.	*Lanius minor*	3 - 5	5 - 8	-	-	-	+	-	A1	-
49.	*Lanius excubitor*	-	8 - 10	6 - 10	-	-	+	-	-	-
50.	*Pica pica*	4 – 5	x	5 - 12	-	-	+	+	A2	-
51.	*Garrulus glandarius*	5 - 6	x	12 - 18	+	-	+	+	A2	-
52.	*Coloeus monedula*	12 - 14	x	3 - 8	-	-	+	+	A2	-
53.	*Corvus frugilegus*	70 - 84	x	48 - 112	-	-	+	+	A2	-
54.	*Corvus cornix*	7 - 9	x	8 - 11	-	-	+	+	A2	-
55.	*Corvus corax*	-	x	2 - 4	+	-	+	-	-	E
56.	*Poecile palustris*	8 - 11	x	x	+	-	-	-	-	-
57.	*Periparus ater*	-	x	3 - 5	+	-	-	-	-	-
58.	*Parus major*	27 - 35	x	x	+	-	-	+	-	-
59.	*Cyanistes coeruleus*	8 - 11	x	x	+	-	-	+	-	-
60.	*Remiz pendulinus*	3 - 5	x	-	-	+	-	-	-	-
61.	*Regulus regulus*	-	-	12 - 15	+	-	-	-	-	-
62.	*Lullula arborea*	3 - 5	x	-	+	-	-	-	A1	-
63.	*Alauda arvensis*	35 - 40	x	-	-	-	+	-	A2	-
64.	*Galerida cristatus*	10 - 13	x	21 - 27	-	-	+	+	-	-
65.	*Riparia riparia*	120 - 132	170 - 230	-	-	+	-	-	-	-
66.	*Hirundo rustica*	x	110 - 320	-	-	+	+	+	-	-
67.	*Delichon urbicum*	x	48 - 64	-	-	+	+	+	-	-

No.	Species	Breeding (pairs)	Migration (individuals)	Wintering (individuals)	Suitable habitats				Birds' Directive	Romanian Red Books
					Forest	Wetlands	Open lands	Villages		
68.	*Phylloscopus collybita*	14 - 18	x	-	+	-	-	-	-	-
69.	*Phylloscopus trochillus*	-	x	-	+	-	-	-	-	-
70.	*Phylloscopus sibilatrix*	2 – 3?	x	-	+	-	-	-	-	-
71.	*Aegithalos caudatus*	-	x	11 - 15	+	-	-	-	-	-
72.	*Acrocephalus arundinaceus*	7 - 9	x	-	-	+	-	-	-	-
73.	*Acrocephalus scirpaceus*	1 - 3	x	-	-	+	-	-	-	-
74.	*Hippolais icterina*	5 - 7	x	-	+	-	-	-	-	-
75.	*Sylvia atricapilla*	10 - 12	x	-	+	-	-	-	-	-
76.	*Sylvia borin*	8 - 10	x	-	+	-	-	-	-	-
77.	*Curruca curruca*	11 - 14	x	-	+	-	+	-	-	-
78.	*Curruca communis*	12 - 15	x	-	-	-	+	-	-	-
79.	*Sitta europaea*	7 – 10	x	x	+	-	-	-	-	-
80.	*Certhia familiaris*	0 – 1?	x	5 - 7	+	-	-	-	-	-
81.	*Troglodytes troglodytes*	1 – 2?	x	7 - 10	+	-	-	-	-	-
82.	*Ficedula hypoleuca*	-	3 – 5	-	+	-	+	-	-	-
83.	*Ficedula albicollis*	0 – 1?	4 – 8	-	+	-	-	-	A1	-
84.	*Ficedula parva*	2 - 3	3 - 5	-	+	-	+	-	A1	-
85.	*Muscicapa striata*	5 – 7	8 - 11	-	+	-	+	-	-	-
86.	*Oenanthe oenanthe*	5 - 6	7 - 11	-	-	-	+	-	-	-
87.	*Saxicola rubetra*	4 - 3	6 - 9	-	-	-	+	-	-	-
88.	*Saxicola rubicola*	2 - 4	4 - 6	-	-	-	+	-	-	-

No.	Species	Breeding (pairs)	Migration (individuals)	Wintering (individuals)	Suitable habitats				Birds' Directive	Romanian Red Books
					Forest	Wetlands	Open lands	Villages		
89.	*Phoenicurus phoenicurus*	6 - 7	x	-	+	-	+	-	-	-
90.	*Phoenicurus ochruros*	8 - 10	x	-	+	-	+	+	-	-
91.	*Erithacus rubecula*	6 - 9	x	-	+	-	-	-	-	-
92.	*Luscinia luscinia*	5 – 6	x	-	+	-	-	-	-	-
93.	*Luscinia megarhynchos*	9 - 11	x	-	+	-	-	-	-	-
94.	*Turdus merula*	12 - 13	x	x	+	-	-	-	A2	-
95.	*Turdus philomelos*	8 - 12	x	-	+	-	-	-	A2	-
96.	*Turdus iliacus*	-	18 – 42	-	+	-	+	-	A2	-
97.	*Turdus viscivorus*	-	52 - 170	-	+	-	+	-	A2	-
98.	*Turdus pilaris*	-	22 - 72	35 - 54	+	-	+	-	A2	-
99.	*Sturnus vulgaris*	x	280 - 1050	0 - 26	+	-	-	+	A2	-
100.	*Passer domesticus*	x	x	x	-	-	-	+	-	-
101.	*Passer montanus*	x	x	-	-	-	-	+	-	-
102.	*Anthus trivialis*	2 - 4	x	-	+	-	-	-	-	-
103.	*Anthus campestris*	5 - 6	x	-	-	-	+	-	A1	-
104.	*Motacilla alba*	4 - 5	10 – 11	-	-	-	+	-	-	-
105.	*Motacilla flava*	9 - 11	14 - 17	-	-	-	+	-	-	-
106.	*Fringilla coelebs*	18 - 23	x	x	+	-	-	+	-	-
107.	*Fringilla montifringilla*	-	-	12 – 78	+	-	+	-	-	-
108.	*Pyrrhula pyrrhula*	-	x	8 - 24	+	-	-	-	-	-

No.	Species	Breeding (pairs)	Migration (individuals)	Wintering (individuals)	Suitable habitats				Birds' Directive	Romanian Red Books
					Forest	Wetlands	Open lands	Villages		
109.	*Coccothraustes coccothrauste*	4 - 6	x	x	+	-	-	-	-	-
110.	*Chloris chloris*	10 - 13	x	-	+	-	-	+	-	-
111.	*Spinus spinus*	-	14 - 32	10 - 25	+	-	+	-	-	-
112.	*Carduelis carduelis*	11 - 14	x	27 - 142	+	-	-	+	-	-
113.	*Acanthis flammea*	-	x	2 - 7	+	-	+	-	-	
114.	*Linaria cannabina*	1 – 3	7 - 9	-	+	-	-	-	-	-
115.	*Emberiza calandra*	11 - 13	x	0 - 2	-	-	+	-	-	-
116.	*Emberiza schoeniclus*	1 - 3	x	0 - 5	-	+	-	-	-	-
117.	*Emberiza citrinella*	6 - 8	x	3 - 16	+	-	-	-	-	-

Legend: Fenology: 1? – Probable breeding species, x – non-estimated population; Birds' Directive: A1 – bird species from Annex 1, A2 – bird species from Annex 2; Romanian Red Books of Vertebrates: V – vulnerable species, E – endangered bird species, CE – critically endangered bird species.

In the perimeter of agricultural lands, in the areas with shrubs and bushes and at the edge of forests we observed three-gamefowl species (*Perdix perdix*, *Coturnix coturnix* and *Phasianus colchicus*) present in the investigated zone. They are polygamous birds, living hidden inside the thicket of vegetation, so their census is difficult; we estimated the breeding population using the males calling activity during the first part of breeding season and the sporadic observation of the birds along the study transects.

We identified nests of the riparian bird species in various sites: the former exploitation loam areas and vertical cracks formed by landslides on the slopes (*Merops apiaster* and *Riparia riparia*) or the high clay bank of the Prut River, especially in the sector Cotul Bran (*Alcedo atthis* and *Riparia riparia*). The sparrows (*Passer montanus* and *Passer domesticus*) occupy often the old nests of sand martins (*Riparia riparia*), especially in the former exploitation loam areas located in vicinity of villages.

We recorded the highest diversity of breeding bird species typical for the aquatic ecosystems inside the meadow forest. The bird species that require reed beds to build their nest and take care of their broods present a low diversity and small populations. We observed these species on the old meanders of the Jijia River, presenting the aspects of puddles with swamp vegetation, and the marshy surfaces are missing in the investigated territory. The regularised sectors of the Jijia River appear as a concrete channel, without suitable breeding habitats from the typical wetlands and aquatic bird species, so the birds use it as resting and feeding territory.

Inside the villages of Golăiești commune, the bird species are building their nests on the walls or roofs of the houses and on the trees along the roads or in the orchards. Some species search their food at long distances from the village area, in the open cultivated lands and grasslands or even in the perimeter of the aquatic ecosystems (*Ciconia ciconia, Hirundo rustica* and *Delichon urbicum* or the two species of *Passer*). Other bird species are not leaving the edge of villages, finding food inside it (*Streptopelia decaocto, Athene noctua* or *Dendrocopos syriacus*).

We met the highest breeding bird species diversity inside and at the edge of the woodlands from the investigated area. We caught some of these bird species far from the edge of the forest, using the shrubs and the clumps of trees less often for nesting but as survey points inside the feeding or hunting territories. The woodpeckers and doves present significant breeding populations but are not leaving the forest to search and find their food; the migratory dove species (*Columba palumbus* or *Streptopelia turtur*) appear searching for food on the cultivated lands area during the month of August. The woodlands passerines present a various trophic regime, but use to feed their chickens with eggs, larvae and adults of insects.

Between the diurnal raptors, two falcon species (*Falco tinnunculus* and *Falco subbuteo*) are breeding, using old nests of crows in clumps of trees. We cannot exclude the possibility of existence of one breeding pair of marsh harrier (*Circus aeruginosus*) in the area. We observed adult and flying juvenile birds during the whole breeding season; probably, they have the nest inside the compact reed beds from one of the meanders of the Old Jijia River.

Two nocturnal raptor species (*Asio otus* and *Strix aluco*) are breeding in the meadow forest from the sector Cotul Bran on the Prut River, but also inside the oak forest from Petreşti – Medeleni. We could not identify their nests, but in June – July we heard the calling sounds of chickens begging the attention of the adult birds who bring food to the nest.

We notice the highest bird diversity during the period of seasonal migration, in spring and autumn, when we counted the biggest bird populations, too; we recorded some bird species in the area only during the migration time, especially in autumn. During the spring migration (March – first decade of May), the birds are going quickly to the breeding areas, the first arrivals occupying the best suitable sites for a high rate of fledging survival. We observed some bird species crossing the area by flight or in short sequences of feeding. In the autumn migration (August – first decade of November), the birds use to stop-over in the suitable feeding and resting areas, preparing themselves for the long way towards the wintering zones. Some migratory bird species can stay even two weeks in the perimeter of Golăieşti commune, using the rich and various food resources and sleeping shelters from the area.

During the late July, the typical forest passerines form larger or smaller flocks, reuniting adult and juvenile birds, flying between the edge of forest and the open lands, arriving to the limits of the villages in search of more abundant and accessible food resources. As example, we can mention species as the warblers – *Sylvia* sp. and *Curruca* sp., flycatchers – *Ficedula* sp., redstarts – *Phoenicurus* sp., finches – *Fringilla coelebs*, *Chloris chloris* and *Carduelis carduelis*. In the late August, we met flocks of hundreds and thousands starlings (*Sturnus vulgaris*) flying towards the south direction or searching for fruits in the area.

This time represents a period of increased mobility even for the sedentary bird species, all the birds searching for food to accumulate fat reserves necessary to survive during the wintering time or to cope with the effort of migration flight. The birds present long daily flights between the forests and shrubs perimeter, used as resting and sleeping shelter sites, respectively the open lands that offer them various types of food resources.

We noticed the passage of the storks (*Ciconia ciconia* and *Ciconia nigra*), sometime in mixed flocks, but the black storks presented significant smaller effectives than the white ones. The two duck species (*Anas platyrhynchos* and *Anas crecca*) appeared on the watercourse of the Prut River, especially in the sector from the neighbourhood of the natural protected area Cotul Bran on the Prut River and in the sector Petrești – Medeleni.

During the wintering time, the populations of waterfowls are small, the birds crowding on the wide meanders of the Prut River with smooth water flow and no ice-bed covering. The constant presence of a high number of diurnal raptors represents the most characteristic element for the wintering bird fauna on the territory of Golăiești commune, including the natural protected area Cotul Bran on the Prut River. The two buzzard species (*Buteo buteo* and *Buteo lagopus*) occupy the hunting territories in the open lands located between the villages and the edge of meadow forests, using solitary trees or shrubs as survey points. We met the merlin (*Falco columbarius*) especially in the trees from the edge of the meadow forest and grasslands.

Two Natura 2000 sites, ROSCI0123 Prut River, respectively ROSPA0163 Prut River present sectors located on the administrative territory of Golăiești commune. Their designation is due to the recorded presence of plant species and animal species included in Annex 2 of the Habitats' Directive [24], respectively, presence of bird species that appear in Annex 1 of the Birds' Directive [25, 26]. These species and habitats need special conservation measures concerning their habitats in order to ensure their survival and the reproduction in their distribution range.

During our monitoring field activity along the common meadow of the Jijia and Prut Rivers on the territory of Golăiești commune, as well as in the area Cotul Bran on the Prut River we identified 21 bird species included in Annex 1 of the Birds' Directive. On the territory of the European Union, these bird species present extinction risk, being vulnerable to the changes of the suitable habitats or becoming rare species due to the diminution of their populations. Most of these recorded species in the investigated area appear with small populations during the migration time as constant presences: *Nycticorax nycticorax, Ardea alba, Platalea leucorodia, Ciconia nigra, Pernis apivorus, Milvus migrans, Milvus milvus, Sterna hirundo* and *Chlidonias hybrid*. One bird species is wintering visitor in this perimeter: *Falco columbarius*. The other 11 bird species are present during the breeding season, two being probably breeding species in the area: *Circus aeruginosus* and *Ficedula albicollis*.

We mention also the presence of 25 bird species included in Annex 2 of the Birds' Directive as gamefowl species; their hunting is regulate through the national laws, but their extraction from ecosystems must keep the species out of the risk of extinction.

In the list of bird fauna recorded in the sector Golăiești – Cotul Bran on the Prut River, we notice 12 bird species that appears in the Red Book of Vertebrates from Romania [27]. From these, the black kite (*Milvus migrans*) is a critically endangered species in our country, presenting high risk of extinction in the near future. We observed two individuals hunting at the southern edge of the natural protected area Cotul Bran on the Prut River in August 2015. Other four species have the status of endangered bird species; between these, only the wryneck (*Jynx torquilla*) is breeding in the investigated perimeter. We met two species (*Ardea alba* and *Platalea leucorodia*) during the migration time and the raven (*Covurs corax*) is present during the wintering time. We identified seven vulnerable bird species: *Ciconia ciconia, Nycticorax nycticorax, Ciconia nigra, Pernis apivorus, Milvus milvus, Streptopelia turtur* and *Upupa epops*. Only three of these species are breeding birds in the area: the white stork (*Ciconia ciconia*), the turtle dove (*Streptopelia turtur*) and the hoopoe (*Upupa epops*).

There are some vertebrate species mentioned in the standard forms of Natura 2000 site ROSCI0123 Prut River [24] that appear also in the Red Book of Vertebrates from Romania [27]. These present status of vulnerable species (fishes: *Gymnocephalus schraetser* and *Zingel zingel*; amphibians - *Hyla orientalis*; reptiles - *Emys orbicularis*; mammals: *Lutra lutra* and *Spermophilus citellus*) or endangered species (*Zingel streber* – from the fishes, respectively, *Myotis myotis* – from the mammals).

The main activities of local community from Golăiești commune are agriculture and breeding of sheep, cattle and goats. The present level of anthropogenic activities is low. We did not met herds of domestic animals inside the forests, but we noticed the intensive extraction – and, probably, illegal - of the wood materials in the forests from the neighbourhood of villages. The owner of the oak forest from the sector Medeleni – Petrești protects this woodland body by digging a peripheral ditch enough deep and wide to prevent the easy access of vehicles inside the forest.

The fishing along the watercourse of the Prut River is possible only with a special document that allows the access in the border area (it is the eastern border of the European Union). The service of Border Police takes a rigorous control of this document, so we noticed the low presence of the sport anglers in the study area. The high and steep bank of the watercourse along the sector of the natural protected areas Cotul Bran on the Prut River is unsuitable for the sport fishing activities.

Between the identified threatening factors in the area, we mention the climate changes and the development of road infrastructure. The prolonged severe drought and the still active classic approach to the flood risk management (concreted banks, dams and drainage) have led to the disappearance of significant wetlands surfaces in the common meadow

of the Jijia and Prut Rivers from this region. The still existent wetlands are subject of disappearance in the near future. The local community faces the lowering of the aquifers' level and water shortage due to the evolution of the aquatic ecosystem in the area.

A significant project of road infrastructure is developing in the area of Golăiești commune, in the neighbourhood of the natural protected area Cotul Bran on the Prut River, aiming to build a new road connection between Romania and the Republic of Moldova. The project includes a bridge over the Prut River and road sectors that will connect the highway Târgu Neamț – Iași – Ungheni and the national road M14 Criva – Briceni – Chișinău – Tiraspol. On the territory of the Republic of Moldova, this road infrastructure project has no impact on a natural protected area. On the Romanian side, one sector of the connection road endangers the natural protected area Cotul Bran on the Prut River, one of the last reproduction refuge for the fish species from the watercourse of the Prut River on the Iași County territory. The first presented environmental impact study has not identified an alternative technical solution to eliminate this risk and has not assessed the collision risk for the fauna present on the territory of protected areas in this perimeter.

4. Conclusions

During two years of monitoring, we identified 117 bird species in the sector Golăiești – Cotul Bran, located in the common meadow area of the Jijia and Prut Rivers, part of the territory of two Natura 2000 sites: ROSCI0123 Prut River, respectively ROSPA0163 Prut River, including the natural protected area Cotul Bran on the Prut River. We recorded the highest diversity of bird fauna inside the woodlands despite the small surfaces covered by forests in the investigated area.

The typical bird species for wetlands and aquatic ecosystems present low specific diversity and small populations, appearing especially during the autumn migration time. Their suitable habitats are present in the perimeter of the former meanders of the Old Jijia River that remained after the hydrotechnic regularisation of the Jijia River, mostly located inside the villages.

In our list of bird fauna, 77 bird species form the regular breeding bird fauna and other six bird species are probably or at least irregular breeding species on the territory of Golăiești commune, including the perimeter of the natural protected area Cotul Bran on the Prut River.

Between the recorded bird species, 21 species appear in Annex 1 of the Birds' Directive as species that need special conservation measures to prevent their extinction on the European Union territory.

During our field activity we met 12 bird species included in the Red Book of Vertebrates from Romania as critically endangered species (one), endangered species (four) or vulnerable species (seven). Other vertebrate species included in this national red list are present on this territory: three fish species, one amphibian species, one reptile species and three mammal species.

The anthropogenic risk factors correlated with the activity of local community present low level of impact for the bird fauna and biodiversity from the region. The climate changes and the projects of infrastructure in the area (highway, roads and bridges) represent the main factors of risk identified for the biodiversity as a whole in the sector Golăiești – Cotul Bran. A correct assessment of the risks is important to find the best technic solutions and to minimize the development impact of this type of projects in this sensitive area.

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The main sources of pollution of Valea Morilor lake which caused the asphygation of fish

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Abstract. The paper illustrates the role of bioindicators applied to identify the sources and degree of pollution of a water basin. The laboratory test reports, standard methodologies and scientific literature considered as an auxiliary tool for the preparation and planning the sampling campaigns for the assessment of the ecological status of the aquatic environment (including sampling, analysis and microscopy) served as support. There were applied the results of the laboratory analyses from the reports on quality indices and technical report, which include qualitative elements of the general physicochemical conditions, hydromorphological and biological qualitative components from Valea Morilor lake.
Keywords: aquatic environment, sources of pollution, negative anthropogenic action, bioindicators, asphyxiation of fish.

Principalele surse de poluare ale lacului Valea Morilor care au provocat asfixarea peștilor

Rezumat. În lucrare este elucidat rolul unor bioindicatori aplicați pentru identificarea surselor și gradului de poluare a unui bazin acvatic. Drept suport au servit rapoartele de încercări de laborator, metodicile tip și literatura științifică considerată drept instrument ajutător pentru pregătirea și planificarea campaniilor de prelevare pentru evaluarea stării ecologice a mediului acvatic, inclusiv prelevarea, analiza, microscopia. S-au aplicat rezultatele analizelor de laborator din roapoartele privind indicii de calitate, raport tehnic, care cuprind elemente calitative ale condițiilor generale fizicochimice, componente calitative hidromorfologice și biologice din lacul Valea Morilor.
Cuvinte cheie: mediul acvatic, surse de poluare, acțiune antropică negativă, bioindicatori, asfixierea peștilor.

1. Introduction

The impact of climate change on the biodiversity of a water basin involves the analysis of the impact on all existing ecosystems in the respective territory and the relationships between them. Disturbance of environmental factors has a direct effect on the evolution of living beings, initially on their ability to adapt and later on their ability to survive. In extreme cases, they are factors for the elimination of certain species on food webs with

drastic consequences on the evolution of biodiversity at the local level and with impact at a general level. To prevent this phenomenon, you need to consider threats, opportunities, recommendations and adaptation measures.

The evaluation of water quality in an aquatic basin and anthropogenic changes in aquatic ecosystems can be carried out by analyzing both abiotic and biotic parameters (using bioindicators). The use of abiotic parameters is more convenient because it directly characterizes the quality of the environment, in particular, concrete negative changes with well-determined quantitative parameters. However, it is impossible to obtain the full characteristic of the environment, the main criterion - the reaction of the biota to the environment - remains unassessed [13].

The advantage of using biotic parameters (bioindication) lies in their great objectivity and validity. The state of the biota is determined by the state (as a whole) of the environment and generally reacts promptly to negative actions of various origins, regardless of evidence and their degree of studies.

Biological testing consists in the use of biological objects, under controllable conditions, for ascertaining and evaluating the actions of environmental factors on the organism and some functions or on a community of organisms.

2. Materials and methods

For the evaluation on 06/09/2022, six water samples were taken from the lake in Valea Morilor Park from Chisinau, in the points where the highest fish mortality rate in the coastal area was detected. The samples were analyzed under the microscope Optica ST-45-2L, Optica B-190TBPL and Optica B-510POL to determine the species that are present. The level of development of phyto- and zooplankton is a good indicator of the sanitary-hygienic quality of the water. In order to identify certain bioindicators, we resorted to:

- visual examination (sample appearance, tubidity);
- organoleptic properties;
- microscopic examination.

The so-called “water bloom” phenomenon can be observed more and more frequently in the lake. Thus, upon the decomposition of organic matter, biogenic substances (simple compounds of carbon, nitrogen, phosphorus) are quickly assimilated by autotrophic organisms (those that photosynthesize), a large part of which belong to algae with saprobic indices: Mougeotia sp. (o – 1.0), *Cymbella ventricosa* Bréb. (x-o–1.33), *Cymbella parva*

(W. Sm.) Kirchn, *Scenedesmus quadricauda* (Hegew.) Hegew. (β – 2.1), *Diatom vulgare* Bory (β-α – 2.4), *Gomphosphaeria lacustris* Chod. (β – 2.0), *Cymbella parva* (W. Sm.) Kirchn., *Achnanthes hauckiana* Grun, *Diatoma vulgare* Bory (β-α – 2.4), *Coelastrum microporum* Näg. (β – 2.1), *Navicula sp*., *Cosmarium venustum* (Bréb.) Archer in Pritchard, *Cymbella parva* (W. Sm.) Kirchn., *Mougeotia sp*. (o – 1.0), *Pediastrum boryanum* (Turp.) Menegh. (o-α – 1.9) (fig. 1-7). They can be uni- or multicellular, colonial or filamentous, usually microscopic. When they develop in large quantities, they can cause the phenomenon of "water bloom", which is expressed by changing the whate colour, pH value, viscosity, transparency decrease, toxic compounds (metabolic products) appearance in the water and the excess of nutrients contributing to the development excessive bacterioplankton, including the pathogenic one [5].

The smell of the water becomes unpleasant (due to the odorous substances produced by algae: geosminte and methyl-isoborneolates) and the lack of dissolved oxygen (used in the process of respiration and decomposition of dead organic matter) can cause mass asphyxiation of fish and other hydrobionts (especially at night when plants consume oxygen as a result of respiration) [13]. About 2000 species of this family are known, but only about 40 are dangerous, due to their relevant toxicity (Anabaena, Oscillatoria, Microcystis, etc.). The composition and abundance of species, and the age structure of fish communities demonstrate irregularities that can be attributed to anthropogenic actions on the physico-chemical and hydromorphological indices of the environmental quality. In some cases, the deficit of reproduction or the development of a certain species can be found, which manifests itself in the absence of certain age groups [7, 8].

3. Results and discussions

In the Republic of Moldova, most of the water resources are polluted, and the natural self-purification processes of water are reduced due to human activities.

The lake from Valea Morilor Park was built in 1950 on an area of 34 hectares, maximum length - 835m and depth of 3.5-5m, perimeter - 2.7 km. The supply is made from the Durleşti river and its tributaries, and from precipitation. This lake presents an aquatic ecosystem characterized by the presence of characteristic species, frequently euconstant, that imprint the specific particularity.

The littoral vegetation at the extremities of Valea Morilor lake is represented insularly by reed *Phragmates australis* (Cav.) Trin.ex Steud. (fig. 9,11), heather *Ceratophyllum demersum* L., *Potamogeton crispus* L., *P.lucens* L., *P.perfoliatus* L., *P.crispus* L., rush *Typha latifolium* L., *T.angustifolia* L., lentil - *Lemna trisulca* L., gorse *Gnaphalium uliginosum* L., rust - *Juncus bufonius* L., watercress *Polygonium hydropiper* L., dogwood -

Figure 1. Microscopy of water sample no. 1 taken from Valea Morilor lake, Chisinau: Mougeotia sp. (o – 1.0); *Cymbella ventricosa* Bréb. (x-o – 1.33); *Cymbella parva* (W. Sm.) Kirchn.; *Scenedesmus quadricauda* (Hegew.) Hegew. (β – 2.1); *Diatom vulgare* Bory (β-α – 2.4).

Figure 2. Microscopy of water sample no. 2 taken from Valea Morilor lake, Chisinau: *Diatom vulgare* Bory (β-α – 2.4); *Gomphosphaeria lacustris* Chod. (β – 2.0).

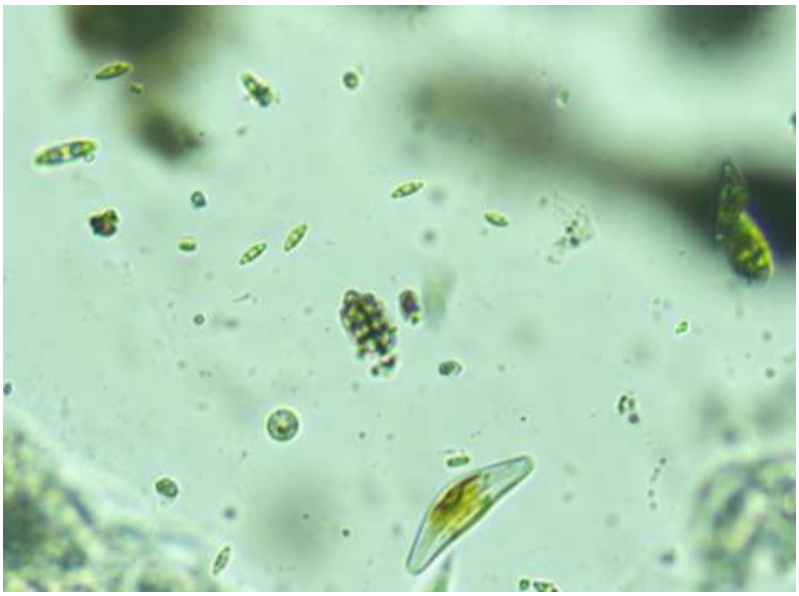

Figure 3. Microscopy of water sample no. 3 taken from Valea Morilor lake, Chisinau: *Cymbella parva* (W. Sm.) Kirchn.; *Achnanthes hauckiana* Grun.

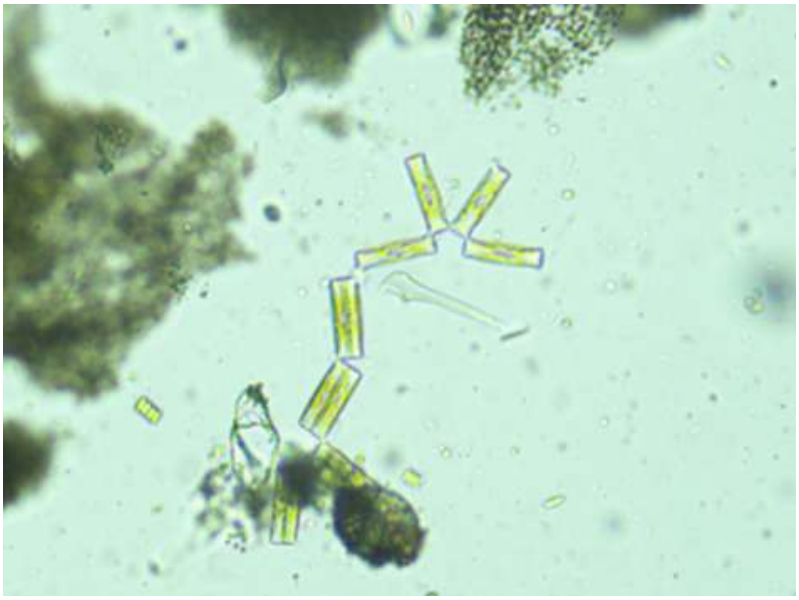

Figure 4. Microscopy of water sample no. 4 taken from Valea Morilor lake, Chisinau:*Diatom vulgare* Bory (β-α – 2.4).

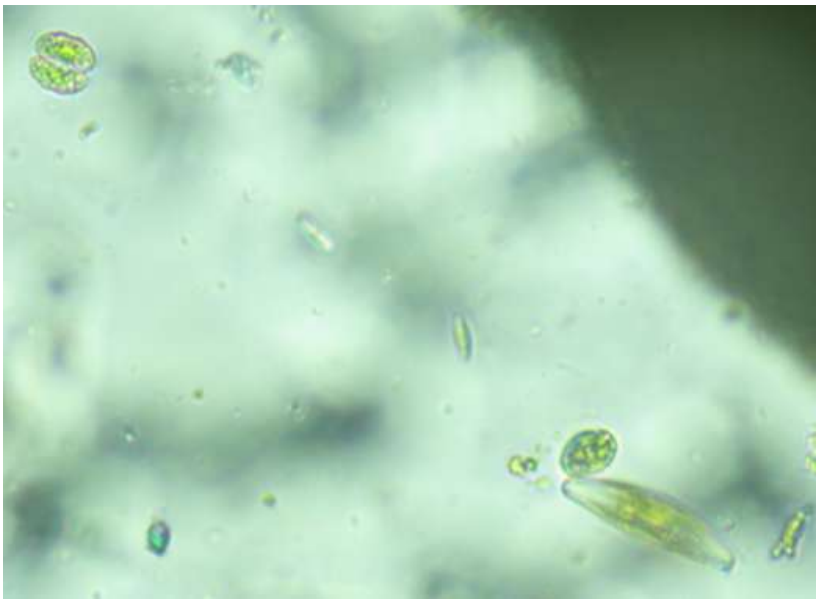

Figure 5. Microscopy of water sample no. 6 taken from Valea Morilor lake, Chisinau: *Navicula sp.*; *Cosmarium venustum* (Bréb.) Archer in Pritchard; *Cymbella parva* (W. Sm.) Kirchn.

Figure 6. Microscopy of water sample no. 6 taken from Valea Morilor lake, Chisinau: *Mougeotia sp.* (o – 1.0).

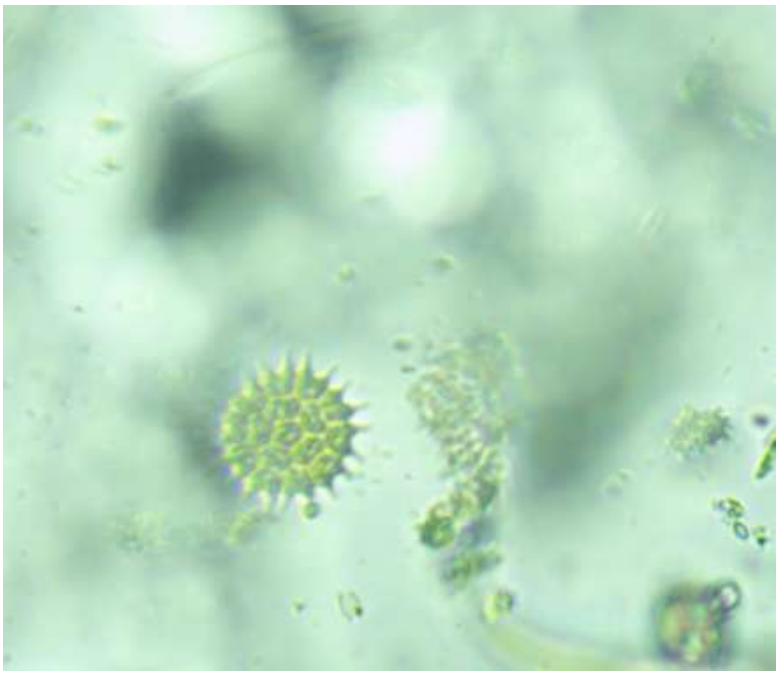

Figure 7. Microscopy of water sample no. 6 taken from Valea Morilor lake, Chisinau: *Pediastrum boryanum* (Turp.) Menegh. (o-α – 1.9).

Bidens tripartita L., etc. Filamentous green algae grow among these plants: *Cladophora glomerata* (L.) Kutz, *Oedogonium sp., Spirogyra sp.*; diatoms - *Nitzschia sp., Cymatopleura sp., Pinullaria sp., Gomphonema sp., Cymbella sp., Rhoicosphenia curvata* (Kutz) Grun, *Achnanthes* sp., while blue algae grow among *Oscillatoria sp., Lyngbya sp.*, *Pseudoanabaena catenata* Boecher, etc. [7]. These strips of aquatic plants develop very intensively during the warm period of the year. The constant presence of these species makes them to be true bioindicators of the aquatic environment. If plant species are permanent and directly characterize the respective biotope, it is much more difficult to identify the presence of animal species and especially meso- and microfauna. And at their level, common species are frequently present, which build up the specific biocenosis.

Biological monitoring is an integral part of ecological monitoring, which provides for the supervision of the environment state regarding physical, chemical and biological parameters, by conducting investigations of the communities of microorganisms, plants, fungi and animals. Thus, numerous species of organisms manifest themselves as natural ecosystems bioindicators, responding to the presence of pollutants in the environment through changes in vital functions, or accumulating pollutants in their bodies. Lake pollution indicators can be differentiated into: sensitive species, which indicate the presence

of a pollutant by the appearance of lesions or malformations, and accumulating species, which concentrate the pollutant in their body [13]. There is also another category of species, which proliferates and becomes abundant under conditions of intense pollution. Pollution indicators can be of animal, fungal or plant origin, the latter being more numerous [1]. It has been established that algae, mosses and lichens are much more sensitive to the action of pollutants than vascular plants, due to the way they absorb nutrients. The species used as bioindicators in the aquatic environment often reflect the trophic situation of the respective environment [8].

For the normal development of the fish in this water basin, it is necessary to take into account a series of conditions:

- the volume of water;
- surface-depth ratio;
- the level of eutrophication (pollution with organic substances) of the aquatic objective;
- the biological productivity of the aquatic objective;
- the chemical composition of the water.

The biological characteristics of water allow it to constitute the vital environment of a whole chain of aquatic organisms, from bacteria and algae to fish. Water is the carrier of biological substances for most organisms. Under the influence of solar energy, the microorganisms in the water at the bottom of the pond mineralize the organic substances that enrich the water following the destruction of bacteria, algae and other hydrobionts, the water being enriched in biogenic elements and mineral salts. When the oxygen concentration is satisfactory, bacteria decompose organic substances into carbon and hydrogen, transforming them into carbonic acid and water; nitrogen from albumin into urea and ammonia. The increased concentration of dissolved oxygen in the lake is due to the presence of algae, which produce oxygen during the day in the process of photosynthesis and consume it at night, causing the fish to suffocate. The Environment Agency, following the laboratory analyses, communicates that this case is a specific one for these freshwater bodies, characterized by the process of water eutrophication (water greening), which leads to an unwanted disturbance of the balance of the organisms present in water and on water quality, especially, by increasing or enriching the organic mass in standing waters.

An important problem is the biological purification of stagnant waters, based on the activity of various organisms, which, following their vital activity, use some pollutants,

and oxidize others with the participation of oxygen which is emitted together with photosynthesis. An important component of this system is bacteria and algae. Bacterial and algal metabolism represent important biological processes that ensure the degradation of organic substances of pollutants together with water purification [6].

On one hand, the development of algae has an important role in the process of biological purification of aquatic objects, on the other hand, algal biomass can be used in the nutrition of invertebrate animals, which represents the initial step of the trophic pyramid. Algae studies have shown that green algae, diatoms and cyanophytes are in the foreground, due to the purifying activity. Of special interest is the ability of algae to concentrate radioactive elements and various inorganic substances, including heavy metals. Dead cells of algae retain accumulated cations and anions no worse than living cells [7]. Along with the mass development of algae in water basins, the rate of quantitative reduction of pathogenic microorganisms essentially increases. Some green, blue algae and diatoms are antagonists of the influenza virus. Algae can even use synthetic detergents as a source of phosphorus. Some algae destroy saccharides, amino acids, pectins, as well as phenols [10].

There are insignificant changes in the composition and abundance of species belonging to the species communities, which can be attributed to anthropogenic actions on the physico-chemical and hydrobiological indices of water quality. The age structure of the fish communities demonstrates irregularities that can be attributed as anthropic actions on the physico-chemical and hydromorphological indices of the environmental quality. In some cases, the deficit of reproduction or the development of certain species can be found, which manifests itself in the absence of a certain age groups.

Currently, a large amount of waste, plastic, plant debris has accumulated in the lake, among which fish die daily. Dozens of dead fish can be seen floating on the surface of the lake.

Due to the high temperatures that are favorable for the development of bacteria and algae, this fact leads to the so-called “blooming” of the water [5]. Phosphorus and nitrogen concentrations also contributed to this. Phosphorus and nitrogen reach the lake water through small streams. Great danger now appears as a consequence of last year blue-green algae death, because, when they decompose, they absorb the oxygen that is in the water and remove toxins that are harmful to other aquatic life, also causing the death of fish [10].

According to specialists, there is a high concentration of nitrogen in the water, but the exact cause of the fish death is not known yet. Over the course of several years, at the same time, according to specialists, this phenomenon occurs because the water is not

Figure 8. The general appearance of the water in Valea Morilor lake, Chisinau (sample 1, 2): a - vegetable remains and dead fish; b – appearance and quality of water.

sufficiently oxygenated. The content of O2 in water varies from 855 to 140%, compared to the saturation norm, being maximum in the summer period, along with the massive development of algal vegetation. Water mineralization oscillates between 700 and 1070 mg/l. The water of the lake belongs to the category of hydrocarbonate-sulfate-chlorine and hydrocarbonate-chlorine-sulfate from the Mg+K and Mg+Na groups, the pH is slightly alkaline. To solve the problem, the municipal authorities proposed to procure 25 aerators, that would activate in addition to the 13 already existing. Later, the specialists took samples that proved that there is insufficient oxygen in water, which leads to the death of the fish.

Eutrophication contributes to the overgrowth of various species of algae in water bodies. The presence of an increased amount of nutrients in water contributes to the intensification of the process of photosynthesis and cell division, which ensures the exaggerated reproduction of algae [5].

Algae-indicators of saprobity in Valea Morilor lake refer to all 4 self-purification groups: xenosaprobe indicates very clean water; oligosaprobe – slightly polluted water, mesosaprobe – water with medium pollution (betamezosaprobe, in which the content of dissolved oxygen is still high, and alphamesosaprobe, with oxygen deficiency) and

polysaprobe – highly polluted (with very little or no oxygen, often rich in ammonia and hydrogen sulfide) (Fig. 1-7).

Figure 9. Fish molting from the Valea Morilor lake, Chisinau (taking samples 3, 4): a - dead fish; b – appearance and quality of water.

Water pollution occurs due to a large concentration of chemical or biological waste that reaches the lake. It is dangerous, posing a great threat to human health.

Some of the most common problems faced by fish species are: insufficient oxygen and organic pollution, thermal pollution, pollution with persistent synthetic compounds, etc. For this, all species characteristic of the habitat type that exploit natural resources in a similar way are taken into consideration, grouping them according to: mode of nutrition, reproduction, tolerability to alternation of environmental gradients, etc. (and serving as input data in the bioindication process); the functional approach - treated through the prism of biochemical, physiological processes, etc. [9].

Due to the recent high temperatures, primary production is increasing. At higher temperatures there is an inhibition of photosynthesis, followed by the quantitative decrease of phytoplankton and primary production, which often leads to the mass death of zooplankton. Also, high water temperatures lead to a decrease in the content of dissolved oxygen in the water, which in turn can cause the death of a large number of fish. Each species is characterized by a thermal interval, having a lower and an upper limit between which the specific life of the group takes place. Within this range, usually wider, there is an

optimum value, always narrower, in which the respective species develops best. Most of the fish species in our waters are eurythermic, withstanding water temperature variations between 0°C and 30-35°C [13].

Aquatic microorganisms are good indicators because they spend all or most of their lives in water, are found in areas where conditions allow their survival, are easy to collect, differ in tolerance to the amount and type of pollution, and are easy to identified in the laboratory. They are good monitoring indices because they live more than a year, have low mobility and are integrators of environmental conditions.

Figure 10. Water sampling points 5, 6 (a, b).

Algae have long been applied as indicators of the state of the aquatic environment and of pollution sources of a water body [6]. As biological indicators, unicellular algae have a number of advantages over other microorganisms. Due to the life cycle, they quickly adapt to the polluted environment or leave life. Identifying correctly the species and appreciating the composition of algocenoses and their population in different water basins, algae serve as reliable witnesses of the quality of the environment. Algal species populations and their communities react quickly to the changes in the chemical composition and other characteristics of the aquatic environment. Diatom algae have the ability to concentrate in their cells heavy metals and radioactive substances from water [5, 14].

In this case, the fish are an indicator of the entire ecosystem, including the presence of species, age characteristics, abundance and their physiological state. Fish are good

indicators because they live in water all their lives, differ in tolerance to the intensity and types of pollution, live for many years and are easy to identify in the field. Individuals and populations of fish generally remain in the same area throughout the summer season; communities are persistent and quickly recover from disturbances in the aquatic environment. Fish represent a very broad spectrum of tolerance from very sensitive to extremely tolerant and show specific responses to chemical, physical and biological degradation of water [9].

If no biological cleaning actions are taken, the lake from Valea Morilor Park in the capital city will turn into "dead water".

The sources of water pollution are varied and can be grouped into:

(1) demographic, dependent on the number and activity of the population in a certain area, being directly proportional to pollution;
(2) urban planning, corresponding to the development of human communities, which use large amounts of water and produce a large volume of waste water;
(3) industrial, dependent on the level of economic, industrial and agricultural development of a region, in the sense of increasing pollution parallel to the intensification of industry [4]. Another problem is micro-plastic pollution, particles that cannot be seen with the naked eye, being also contained in hygiene and washing products.

This micro-plastic ends up in water with discharge of waste water. Pollution also occurs through plastic bags that end up in water bodies.

Currently, water quality assessment based only on physico-chemical parameters does not always provide complete information on the effects of pollution on aquatic organisms or on the health status of the respective ecosystem. The representatives of the Laboratory for Water Quality within the Environment Agency took water samples from the lake in Valea Morilor park in order to determine the quality of the surface water, according to the analysis indices - pH, dissolved oxygen (O2), suspended matter (MS), consumption chemical oxygen (CCO-Cr), biochemical oxygen consumption (CBO5), ammoniacal nitrogen (N/NH4), nitrites (NO2), nitrates (NO3), total phosphorus (Ptotal). According to the physical-chemical test report, the water of the lake is attributed to the IV quality class (polluted, according to the environmental quality requirements for surface waters, regulated in the Decision of the Government of the Republic of Moldova no. 890 of 12.11.2013, Annex no. 1) [4].

The effect of the influence of heavy metals on hydrobionts, from the necessary and vitally important concentration to the toxic and even lethal concentration, can be in a very narrow range of values, moreover, some and the same concentrations can be

optimal for a group of hydrobionts and lethal for another. The same concentration can have special effects in different aquatic ecosystems, even in the same ecosystem, but in different circumstances of environmental parameters (water hardness, pH, dissolved oxygen, presence of antagonistic or synergistic elements, temperature, etc.) [13].

In most cases, in the natural aquatic ecosystems of the Republic of Moldova, we are faced with sub-lethal concentrations of pollutants (with the exception of the observed stichinic cases where the large amount of pollutants and the short time of diversion cause catastrophic ecological conditions). Namely, these negative changes, which give "at first glance" invisible reactions and appear at various levels of organization, must be promptly identified and correctly interpreted. Particular attention in the monitoring process is given to the action of toxicants on the fish fauna. If an ecosystem is subjected to multiple chemical stressors, the indicator species approach is difficult because they respond differently to different sets of stressors [4].

The species used as bioindicators in the aquatic environment are unique environmental indicators to the extent that they provide a signal on the biological condition in the aquatic environment. Using bioindicators as an early way to detect pollution or ecosystem degradation can help to maintain critical resources. Although the term indicator species is frequently used, it is somewhat inappropriate, as indicators are actually groups or types of biological resources that can be used to assess the state of the environment [2].

The estimation of the quality of the environment can be carried out not only on the basis of species hypersensitive to the modification of environmental factors, but also by the presence in the hydrobiotope of some species resistant to pollution, their abundance serving as an indicator of the unfavorable ecological state. Thus, the phenomenon of bioinvasion can serve to evaluate the quality of aquatic ecosystems. Pollutants affect aquatic organisms and primarily act on the diversity, structure and production capacity of phytoplankton. In the conditions of high toxicity, but with a sublethal effect, there is a decrease in the numbers of all age groups, only tolerant individuals with a slow growth rate are selected (for example in the intensely polluted areas of the lake) [11]. Under the conditions of high concentrations of nutrients and high temperatures in the water basins of the municipality of Chisinau, the rapid multiplication of algae species from the genera Anabaena, Aphanizomenon, Oscillatoria, Microcystis, Euglena, Trachelomonas etc., which sometimes causes the phenomenon of "water blooming" [3].

Phytoplanktonophagous fish are used to combat the "water bloom" phenomenon. Thus, the inclusion of algal biomass in the nutrition of phytoplanktonophagous fish becomes useful for the functionality of the ecosystem, reducing the negative risks caused by this phenomenon. A biological, effective and harmless method of preventing this dangerous

phenomenon is the breeding of the blood carp, also called the silver carp (*Hypophthalmichthys molitrix*). Due to its very fine gill filter, it can retain particles of 0.35-0.45mm, mostly formed by planktonic algae from all categories, including cyanophytes, zooplankton and organic detritus. Thus, the inclusion of algal biomass in the nutrition of phytoplanktonophagous fish leads to the reduction of fish asphyxia, caused by the phenomenon of "water bloom" [5].

Macrophytes are also beneficial to lakes because they produce oxygen, are a source of food for certain organisms, provide substrate for aquatic invertebrates and camouflage for fish. A lake without macrophytes suggests a reduction in fish populations, or water quality problems as a result of excessive turbidity, the presence of pollutants. Macrophytes are excellent indicators of aquatic ecosystems because they react to nutrients, toxic contaminants, metals, herbicides, turbidity and water level [2].

Many researchers have tried to use these structural indices as tools for monitoring and evaluating the state of ecosystems, because they express some quantitative ratios and some grouping relationships between the species of a biocenosis that, thus, allow a more complete and correct characterization of the structure and role of different species in the biocenosis activity, as well as the comparison of the biocenoses with each other (in our case, the ichthyocenoses).

Aquatic ecosystems are particularly affected by chemical stress due to the tendency of pollutants to distribute themselves homogeneously and rapidly in the active mixing zone. Under these conditions, changing the chemical characteristics of the environment will eliminate some sensitive species and will favour others that are more toxic-resistant. Chemical stress can be expressed by the replacement of "more competitive but more sensitive" species by stress tolerant species. In some cases, a true "blooming of opportunistic species" may occur, which are normally excluded or are marginalized by competition or predation. In the current ecological conditions, when the anthropic pressure is continuously maintained on natural aquatic ecosystems, demonstrating an already chronic character, and the most noticeable changes are those at the level of the ichthyocenosis structure.

The use of bioindicators in ecological forensic expertise is motivated by the direct determination of biological effects, synergistic or antagonistic effects of multiple pollutants on an organism, allowing the rapid recognition of the effect that the pollutant has on organisms, including humans, and the relatively low cost compared to other methods. Bioindicators are differentiated into accumulation bioindicators (they store pollutants without manifesting metabolic changes, accumulative indicators are often considered

biomonitors) and response bioindicators (they react through cellular changes or visible symptoms even to small amounts of substance) [12].

In order to obtain a more complete picture regarding the state of water quality, the evaluation must also be extended to the biological components that can store information at a structural and functional level, in time and space, etc. [11]. It is almost impossible to achieve an integrated monitoring of abiotic and biotic parameters even in the simplest structured ecosystem, therefore, one of the most important objectives is to replace, as efficiently as possible, the complicated, painstaking, too expensive and often time-consuming measurements with "delayed effect" with long-term research. Various groups of living things (from bacteria to mammals) are used to monitor the health of the environment and investigations are carried out at different levels of integration and organization of life (from intracellular to supra-population). The ecobiological indication of water quality allows the express assessment of the level of pollution of the aquatic environment, presenting an advantage for forensics in the framework of ecological forensic expertise that requires a quick assessment [12]. The rapid assessment of the quality of the aquatic environment is becoming more and more effective and current.

4. Conclusions

Based on the results of scientific research, it should be noted that the risk of pollution of the lake in the Valea Morilor park admits that human activities can generate certain forms of modification of this ecosystem through these activities and the storage of waste (from construction, housekeeping, etc.), affecting considerably flora and fauna. This environmental degradation represents both a disaster risk factor and a cause for increasing the vulnerability of plant, animal and microorganism communities. The numerical increase of algae species in the lake indicates a drastic risk of pollution in recent years.

Through their vital activity, planktonic algae contribute to the biological productivity of aquatic ecosystems, regardless of whether the percentage of participation in it is high or low, and they constitute a part of animal food at different trophic levels. The study of phytoplankton photosynthesis intensity is necessary for estimating the biological productivity of aquatic ecosystems, determining the legitimacy of biotic transformations of matter and energy, and developing recommendations for the rational exploitation of aquatic ecosystems. In biomonitoring systems, planktonic algae play a special role as bioindicators with a high sensitivity to physico-chemical changes in the environment and the degree of organic loading. Currently, the self-purification index is increasingly used to determine water quality - the ratio of gross primary production to the summary destruction of plankton.

Pollutants have a direct negative influence at various levels of integration and organization of life from the molecular to the organismic level - growth retardation, various forms of pathologies, the reduction of reproductive capacity up to the death of the organism and the definitive disappearance of sensitive species. Thus, water pollution decreases the longevity of living organisms (flora, fauna) and leads to the disappearance of species in large proportions or to the disappearance of the entire ecosystem.

Currently, the express control of the quality of the aquatic environment, by means of ecobioindicator organisms, is becoming more and more current, in connection with the diversification and increasing dimensions of the changes taking place in nature. The use of eco-bioindicator objects has several advantages over the technical, chemical and organoleptic methods of assessing the state of the biological components of ecosystems.

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Synthesis and study of coordinating agents for the synthesis of new coordination compounds

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Abstract. Two compounds were obtained from the condensation reaction of semicarbazide (hydrazinecarboxamide) and semithiocarbohydrazide (hydrazinecarbothioamide) compounds with a 3-pyridinecarboxaldehyde carbonyl compound: (E)-1-(pyridin-3-ylmethylene)thiourea (L-1) and (E)-1-(pyridin-3-ylmethylene)urea (L-1) (L-2). The structure and composition of these compounds were determined using theoretical calculations with the GAMESS software package and IR spectroscopy. The new organic molecules L-1 and L-2 have the potential to be used as mono- or bidentate coordinating agents in the construction of coordination compounds with various useful properties.
Keywords: bridging ligand, coordinating compound, synthesis, condensation, hydrazinecarboxamides, hydrazinecarbothioamides, carbonyl compound, IR spectrum, spectrophotometry, GAUSSIAN, theoretical calculations.

Sinteza și studiul unor agenți de coordinare pentru sinteza noilor compuși coordinativi

Rezumat. În baza reacției de condensare dintre compușii semicarbazida (hydrazinecarboxamide) și semitiocarbohidrazida (hydrazinecarbothioamide) cu un compus carbonilic 3-piridincarboxaldehidă au fost obținuți doi compuși: (E)-1-(pyridin-3-ylmethylene)-thiourea (L-1) și (E)-1-(pyridin-3-ylmethylene)urea (L-2). Structura și compoziția acestor compuși a fost descifrată în baza calculelor teoretice folosind pachetul de programe GAMESS, cât și prin intermediul spectroscopiei IR. Moleculele organice noi L-1 și L-2 prezintă perspective de utilizare în calitate de agenți de coordinare mono- sau bidentați cu scopul asamblării compușilor coordinativi cu diverse proprietăți utile.
Cuvinte cheie: ligand punte, compus coordinativ, sinteză, condensare, hydrazinecarboxamidă, hydrazinecarbothioamidă, compus carbonilic, spectru IR, spectrofotometrie, GAUSSIAN, calcule teoretice.

1. Introduction

One of the branches of modern chemistry that offers the possibility of obtaining numerous coordination compounds with predetermined properties is coordination compound chemistry. The methods for obtaining coordinating compounds can be varied by changing

the metal atoms, the nature of ligands, the sets of atoms that can participate in coordination, the nature of the chemical bonds, the intermolecular interactions and the diversity of the structures that these compounds can form among other things. The structure of the coordinating compound can be influenced by using different ligands and the modification or choice of optimal synthesis conditions will condition the arrangement of structural units in space and the properties of obtained products.

At the moment, an important direction in Materials Science is the synthesis of new chemical compounds with useful properties for various fields of industry. Synthetic precursors (different ligands) are later used in the synthesis of vitally important coordinating compounds.

A neutral ion or molecule is traditionally defined as a ligand that is directly attached around a central ion or atom. Thus, we can admit that ligands are coordinating atoms or groups of atoms that contain one or more coordinating atoms (donors, ligates, ligators, or binders) that are directly attached to a nuclear or central atom. Multidentate (polydentate) ligands are groups that contain more than one potential coordinating atom. If a ligand is attached to a central atom via two or more coordinating atoms, it is referred to as a chelate ligand; if it is attached to more than one coordination center, it is referred to as a bridging group or a link group [1].

Obtaining useful compounds is focused on various methods of chemical synthesis of new complexes with composition, structure and manifested useful properties. Later, these compounds are subjected to qualitative composition and structure determination using modern physical methods of analysis, theoretical study of the energy state of molecular systems, analysis of some of them as stimulators of biosynthesis processes of enzymatic preparations, gas traps and so on.

Quantum-chemical calculations, which allow to calculate the energy of these systems, predict the direction of some reactions (e.g. condensation reactions), the mechanisms of substitution and so on; are a useful mechanism for understanding some phenomena and processes that occur in simple and complex molecular systems. These methods can be used to decipher and model the structure of the investigated compounds by comparing the results to theoretical data. Different research methods are employed. Some of them are based on the use of several programs, one being GAMESS, which contains various calculation methods, beginning with those of molecular dynamics and mechanics, semi-empirical methods, ab initio methods based on the Hartree-Fock theory, or methods based on density functional theory and can be used to calculate a wide range of molecular properties [2]. Furthermore, powerful instrumental methods such as IR spectroscopy and

nuclear magnetic resonance (NMR) can be used to decipher the composition and structure of the synthesized ligands.

Infrared spectroscopy (IR spectroscopy) is a spectroscopic technique that studies the interaction of infrared radiation with matter. Infrared spectroscopy employs a variety of techniques, the majority of which are based on absorption spectroscopy. Its applications include the identification and study of specific compounds in solid, liquid, or gas samples.

A molecule must be IR active, i.e. have a specific vibration in order to absorb in the IR range. Molecular vibration is associated with changes in the dipole moment, so the molecule does not have to be a permanent dipole to occur [3].

Compound identification using infrared spectra is so safe and convenient that it has largely replaced older methods based on melting point, refractive index and so on. Its main advantage is the certainty of the conclusion even for partially impure materials; one disadvantage is the space required to unfold all of the details of a spectrum.

Nuclear magnetic resonance (NMR) is a physical phenomenon based on the quantum mechanical properties of atomic nuclei. It should be noted that due to NMR experiments are performed on atom nuclei rather than electrons, the information provided refers to the spatial positioning of these nuclei in the studied chemical compound, which is based on an intrinsic property known as spin. NMR is a property of atomic nuclei with nuclear spins (e.g. ^{1}H, ^{13}C, ^{17}O, ^{19}F, ^{31}P, ^{129}Xe ...) in a magnetic field. When exposed to electromagnetic (radiofrequency) radiation, most commonly in the form of pulses, atomic nuclei can absorb the energy and then release it during relaxation.

Depending on the magnetic field and other molecular factors, the energy delivered during this resonance phenomenon corresponds to a very precise frequency. As a result of this phenomenon, the quantum magnetic properties of nuclei in gas, liquid, or solid phases can be noticed. As a result, only atoms with magnetic nuclei exhibit the resonance phenomenon [4].

When investigating a newly synthesized structure in organic chemistry, NMR spectrometry represents the method with the greatest potential for structural elucidation. NMR spectrometry is an investigative technique that requires minimal sample preparation in advance and provides the ability to obtain quantitative and qualitative structural information for any molecule characterized by atoms with a nuclear kinetic moment.

2. Methodology of the experiment

The ligands **(E)-1-(pyridin-3-ylmethylene)thiourea (L-1) and (E)-1-(pyridin-3 -ylmethylene)urea (L-2)** were obtained as a result of the condensation reaction between

the compounds semicarbazide (hydrazinecarboxamides) or semithiocarbohydrazide (hydrazinecarbothioamides) with a carbonyl compound – 3-pyridinecarboxaldehyde (Figure 1).

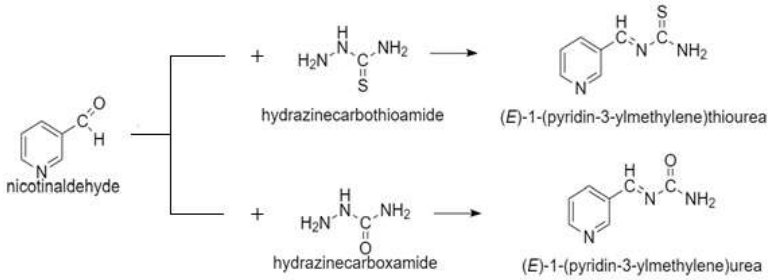

Figure 1. Scheme for obtaining the ligands L-1 and L-2

Following the condensation reaction between the compounds 3-pyridinecarboxaldehyde (nicotinaldehyde) and hydrazinecarbotiamide, the bridging ligand **(E)-1-(pyridin-3-ylmethylene)thiourea (L-1)** was obtained (semithiocarbazide). The semithiocarbazide (2.88 g, 31 mmol) was dissolved (CH_3CN) in 40 mL of H_2O and 10 mL of acetonitrile.

At a temperature of about 35°C, it was magnetically stirred for 45 minutes before adding 3.15 mL of 3-pyridinecarboxaldehyde dropwise. The precipitated pale yellowish product was filtered, washed in 50 mL of C_2H_5OH, and dried at room temperature. The dry precipitate was weighed and found to have a 50% yield.

The second bridging ligand **(E)-1-(pyridin-3-ylmethylene)urea (L-2)** was also obtained as a result of the condensation reaction between 3-pyridinecarboxaldehyde (nicotinaldehyde) and semicarbazide. Semicarbazide (1 g, 7.5 mmol) was dissolved in 50 mL H_2O under magnetic stirring, adding 1.3 mL 3-pyridinecarboxaldehyde dropwise, then the temperature of the solution was raised to about 50°C, stirring for 2 hours. After stirring, the solution was left for crystallization for 72 hours.

The obtained precipitate was filtered, washed in 50 mL of C_2H_5OH and was left to dry at room temperature for 48 hours. The white precipitate was weighed, giving a yield of 44%.

3. Results and discussions

High-performance instrumental methods such as IR spectroscopy, which is the most suitable method for identifying functional groups in the structure of organic compound molecules, were used to decipher the composition and structure of the synthesized ligands. Infrared radiation (IR) is a region of the electromagnetic spectrum that includes the visible and microwave regions and has wavelengths of the order of 10^{-5} m.

Wavelengths in the 2.5-25 μm range are used to record IR spectra in order to determine the structure of organic compounds (most often the wave numbers cover the range 400-4000 cm^{-1}). An IR spectrum contains absorption bands caused by vibrations that occur simultaneously with the participation of all atoms in the molecular structure (normal vibrations) of the analyzed organic compound. The position of an absorption band formed by vibrational excitation of a particular functional group in the spectrum is well defined, varying within narrow limits with the environment of functional group within the molecule. An absorption band characteristic of the same functional group is found at almost the same wavenumber value in the IR spectrum of any molecule (characteristic group vibrations). This fact enables the identification of a molecule's component structural elements by assigning characteristic absorption bands in the IR spectrum [5].

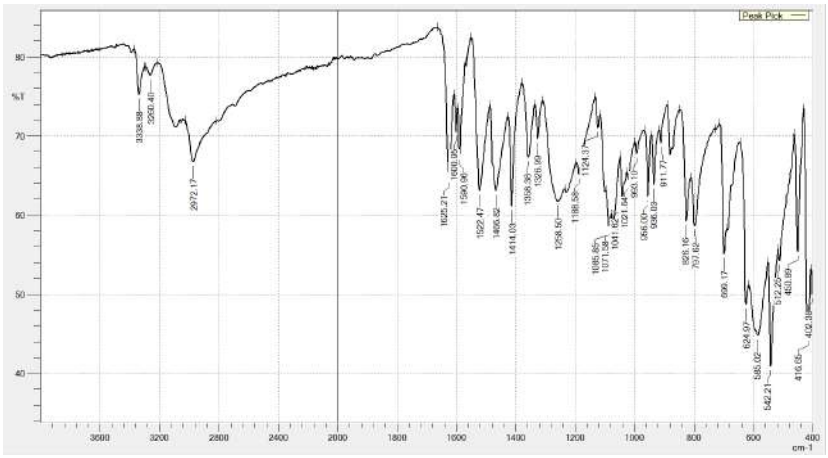

Figure 2. IR spectrum of the L-1 ligand

The IR spectrum (Figure 2) shows the presence of functional groups characteristic of compound L-1, as assigned in Table 1.

At the same time, theoretical calculations for the L-1 and L-2 ligands were done, obtaining the most energetically stable geometric structure. The calculations were carried out using the GAUSSIAN set of modern programs, the DFT theory and the standard 6-31G basis set. The theoretical vibrations of the functional groups shown in Figure 3 and Figure 6, as well as the theoretical wavelengths shown in Table 2 and Table 4, were obtained.

The presence of various electron-donating atoms in the L-1 compound, such as the nitrogen atom of the pyridine ring, the nitrogen atom of the amine group, the sulfur atom, and so on, allows to formulate the hypotheses regarding the compound's potential use as a monodentate and bidentate (bridging) coordinating agent.

Table 1. Functional groups and wavelengths characteristic of ligand L-1

Functional groups	Practical wavelength
C=S	1258.5 cm^{-1}
N-C-N	1071.58 cm^{-1}; 1085.85 cm^{-1}
C-H:C=C:C=N	797.62 cm^{-1}; 826.16 cm^{-1}
The ring vibrations	1590.96 cm^{-1}, 1600.95 cm^{-1}
C-H	2972.17 cm^{-1}
NH2	3260.40 cm^{-1}; 3338.88 cm^{-1}

Table 2. Functional groups and theoretical wavelengths assigned to the ligand L-1

Functional groups	Theoretical wavelength
C=S	1300.78 cm^{-1}
N-C-N	1044.82 cm^{-1}; 1074.33 cm^{-1}
C-H:C=C:C=N	704.11 cm^{-1}; 738.70 cm^{-1}; 909.64 cm^{-1}
The ring vibrations	1603.35 cm^{-1}; 1635.35 cm^{-1}
C-H	3125.93 cm^{-1}
NH2	3591.06 cm^{-1}; 3731.09cm^{-1}

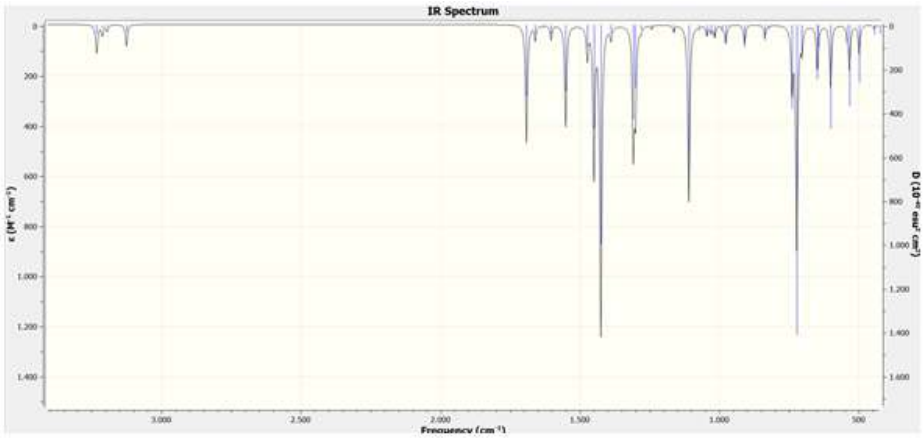

Figure 3. Theoretical spectrum of the L-1 ligand

The L-1 bridging ligand molecule is illustrated in Figure 4 and the L-2 ligand molecule is illustrated in Figure 7.

The presence of functional groups characteristic of compound L-2, as assigned in Table 3, can be seen in the IR spectrum (Figure 5).

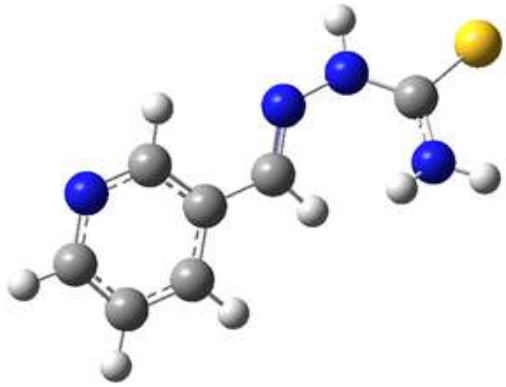

Figure 4. The ligand molecule L-1

Table 3. Functional groups and wavelengths characteristic of the ligand L-2

Functional groups	**Practical wavelength**
C=O	1672.29 cm^{-1}
N-C-N	1050.18 cm^{-1}; 1090.13 cm^{-1}
C-H:C=C:C=N	769.08 cm^{-1}; 811.89 cm^{-1}
The ring vibrations	1589.53 cm^{-1}
C-H	3074.91 cm^{-1}
NH2	3193.34 cm^{-1}; 3338.87 cm^{-1}

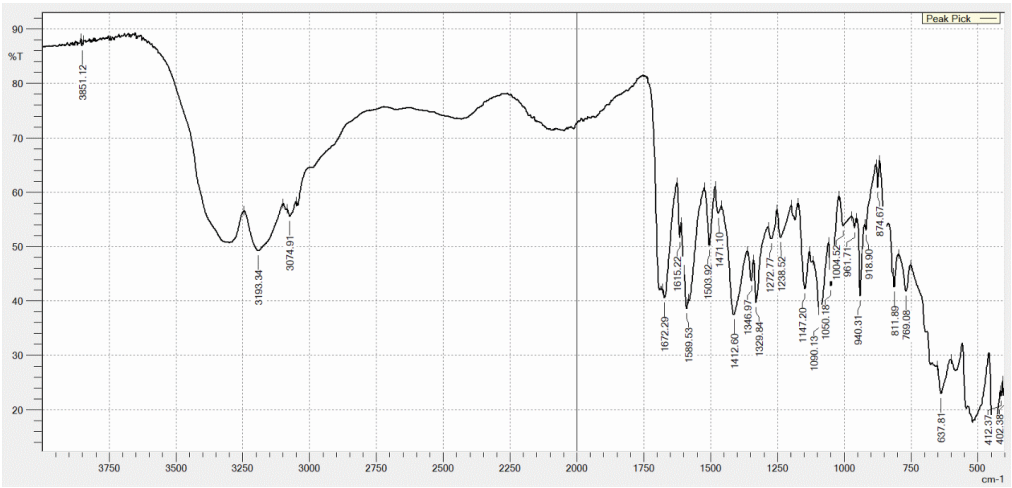

Figure 5. IR spectrum of the ligand L-2

Table 4. Functional groups and theoretical wavelengths assigned to the ligand L-2

Functional groups	Theoretical wavelength
C=O	1745.19 cm^{-1}
N-C-N	1073.52cm^{-1}; 1125.56cm^{-1}
C-H:C=C:C=N	737.38cm^{-1}; 880.92cm^{-1}
The ring vibrations	1604.81 cm^{-1}; 1635.79 cm^{-1}
C-H	3125.67 cm^{-1}
NH2	3613.34cm^{-1}; 3748.41 cm^{-1}

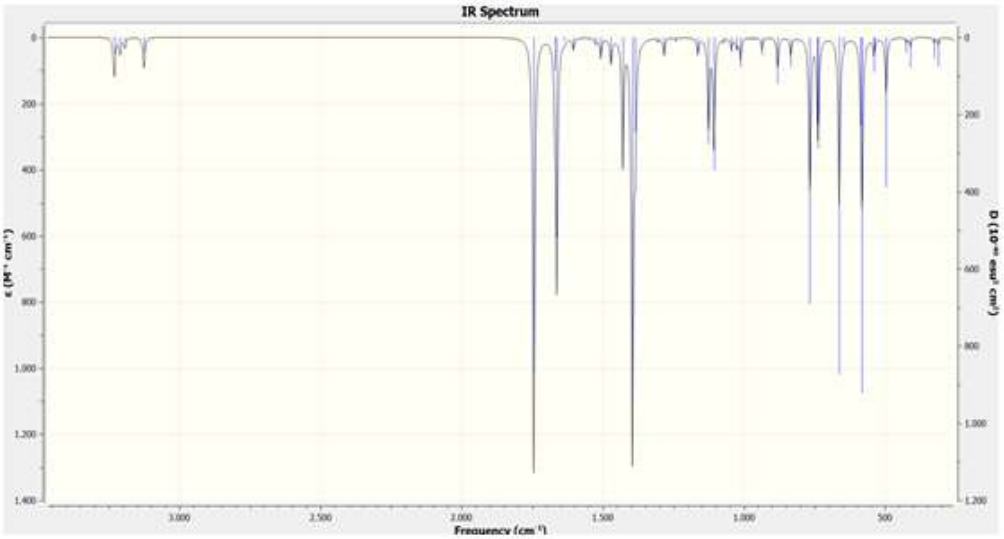

Figure 6. Theoretical spectrum of the L-2 ligand

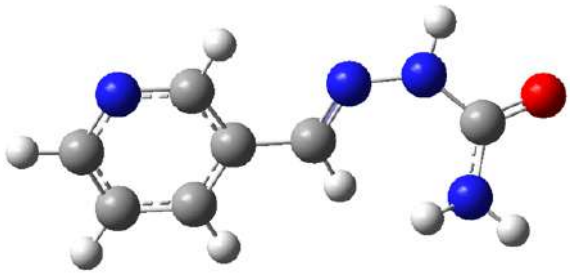

Figure 7. The L-2 ligand molecule

Compound L-2, like L-1, has a set of electron-donating atoms capable of forming coordinate bonds, the only difference being the sulfur atom replaced by an oxygen atom.

Analysis methods such as IR spectroscopy and a set of modern GAUSSIAN programs were used to determine the composition and structure of the obtained compounds.

4. Conclusions

The primary findings of this study are the development of methods for the synthesis of two ligands based on the condensation reaction of compounds as semicarbazide (hydrazinecarboxamides) and semithiocarbohydrazide (hydrazinecarbothioamides) with the carbonyl compound 3-pyridinecarboxaldehyde. Two compounds were obtained: (E)-1-(pyridin-3-ylmethylene)thiourea (L-1) and (E)-1-(pyridin-3-ylmethylene)urea (L-2). The structure and composition of these compounds were determined using theoretical calculations with the GAMESS software package, as well as by means of IR spectroscopy.

The ligands will then be described using nuclear magnetic resonance (NMR) to specify their composition and structure before being used in the synthesis of coordination compounds of transition metals (Zn, Cd, Fe, etc.) with useful properties for agriculture and industry.

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Use of natural pigments obtained from cyanobacteria and algae

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Abstract. The article reflects data on the use of cyanobacteria pigments in cosmetology. One of the sources of natural antioxidants are the pigments obtained from various algae and cyanobacteria. An essential source for extracting pigments and biologically active substances used in cosmetology, pharmaceuticals, etc. is represented by algae and cyanobacteria. Also, the extracts from cyanobacteria have an important role in the anti-wrinkle effect. Useful pigments include: carotenoids, xanthophylls, astaxanthin, fucoxanthin, chlorophyll, phycoerythrin.
Keywords: carotenoids, xanthophylls, astaxanthin, fucoxanthin, chlorophyll, phycoerythrin, cosmetology.

Utilizarea pigmenților naturali obținuți din cianobacterii și alge

Rezumat. Articolul reflectă date despre utilizarea pigmenților de cianobacteri în cosmetologie. Una dintre sursele de antioxidanți naturali sunt pigmenții obținuți din diverse alge și cianobacterii. O sursa esentiala pentru extragerea pigmentilor si substantele biologic active folosite in cosmetologie, farmaceutice, etc reprezinta algele si cianobacteriile. De asemenea, extractele din cianobacterii au un rol important in efectul antirid. Pigmenții utili includ: carotenoizii, xantofilele, astaxantina, fucoxantina, clorofila, ficoeritrina.
Cuvinte cheie: carotinoizi, xantofile, astaxantina, fucoxantina, clorofila, ficoeritrina, cosmetologie.

1. Introduction

Nowadays, consumers' desire for organic cosmetics has increased substantially, as synthetic products cause multiple adverse effects and possess a much lower absorption rate due to large molecules. Thus, algae and cyanobacteria such as Spirulina platensis have gained particular importance in the cosmetic industry. They have beneficial effects on the dermis, being a source of biologically active substances [1].

Carotenoid production by *Spirulina platensis* has often been experimentally stimulated under different stress conditions such as high salinity and nitrogen deficiency. Exposure of *S. platensis*. Carotenoid and B-carotene content has been shown to increase at high levels of saline and nitrogen deficiency. The increase in carotene content in cyanobacterial

cells can be attributed to the excessive formation of free radicals under stress conditions, produced to protect the cells and to continue their growth [2].

From the multitude of substances extracted from cyanobacteria, Carotenoids are listed, which are yellow or orange pigments whose chain ends with ionic rings, being biosynthesized in increased quantities by a large part of photosynthesizing cyanobacteria [3].

Chemically, carotenoids are non-oxygenated organic compounds such as α-carotene, β-carotene and lycopene, or oxygenated hydrocarbons such as lutein and astaxanthin. Due to the keto or hydroxyl terminations at the ionone ring, carotenoids possess antioxidant properties [4].

This type of pigments are fat-soluble, which provide protection to the skin against UV rays, at the same time they inhibit the synthesis of melanin, being strong antioxidants. Marine microalgae also contain about 0.2% carotenoids. In cosmetology, β-carotene is the main ingredient of balms, shampoos, aftershave lotions, which are of biotechnological interest in extracting this compound [9].

2. Obtained results and discussion

The main sources of carotenoids are, in addition to cyanobacteria, microalgae from the Chlorophytaceae family. Species of the genus Dunaliella, for example, have a high content of β-carotene, and *Hematococcus pluvialis* contains a high level of xanthophylls (astaxanthin).

A promising biotechnological source are xanthophyte microalgae, which synthesize (violaxanthin, antheraxanthin, zeaxanthin, neoxanthin and lutein) and can also produce other biologically active substances, such as astaxanthin (figure 1), loroxanthin and caraxanthin. For example, brown algae and diatoms produce fucoxanthin, diatoxanthin [2].

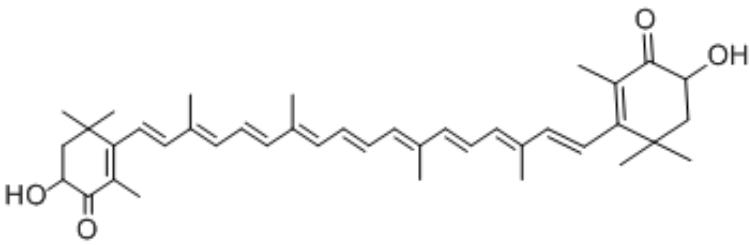

Figure 1. Structural formula of the astaxanthin compound

Astaxanthin (Figure 1) is a red carotenoid pigment that possesses both ketone and hydroxyl groups, it shows more intense antioxidant properties than vitamin E and β-carotene [3]. As an antioxidant it scavenges free radicals and protects the lipid bilayer

from peroxidation and inhibits H_2O_2- mediated activation of the NF-jB transcription factor.

Astaxanthin extracted from Hematococcus pluvialis shows effective protection against UV rays, also shows some improvement against wrinkles as well as improves skin texture, blocks the production of pro-inflammatory cytokines. It is known that this pigment also possesses skin depigmentation properties, it inhibits melanin synthesis by 40% [9]. Based on biotechnological progress, Fujifilm Corporation has created a product based on the astaxanthin pigment "Astalift Whitening Essence", this product is effective in combating skin spots that appear during aging. Kose is another company that has marketed astaxanthin that fights both wrinkles and blemishes on the skin. The Swedish company AstaReal AB has marketed astaxanthin in the AstaReal cream, which helps to revitalize the skin, removes wrinkles and also gives skin elasticity. In 1996 Arad and Yaron developed eye shadow, lipstick in the form of powders or creams obtained from some emulsions of red microalgae [3].

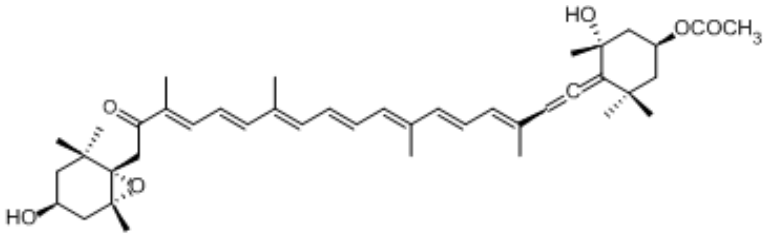

Figure 2. Structural formula of the compound fucoxanthin

Fucoxanthin (Figure 2) is a pigment that contains the hydroxyl group in the ionic ring, it is brown or olive-green in color. It contributes to the photosynthesis process in brown algae such as Sargassum saliquastrum by absorbing red light[4], acquired from them which exhibits antioxidant properties against cell damage induced by hydrogen peroxide.

It has been observed that fucoxanthin obtained from Laminaria japonica inhibits the activity of tyrosinase and melanogenesis, which is a method of skin whitening, because it limits the speed of pigmentation [3,15]. Likewise, this pigment hydrates the skin and maintains the functionality of the skin cells, the softness of skin, anti-wrinkle effect, as well as anti-inflammatory effect [6]. The main bioactivities of fucoxanthin are: antimalarial, antitumor, anti-obesity, anti-inflammatory and antidiabetic [15, 16]. From a pharmaceutical point of view, this pigment has protective effects on the brain, liver, blood vessels, bones and eyes; in creams it has revitalizing effects on the dermis [6]. The companies Unilever, L'Oreal, Henkel and Beiersdorf will improve the growth of the carotenoid market value in the European market due to the properties they possess [14].

Laminaria digitata Isochrysis spp., *Postelsiapa maeformis* and species of the genus Nostoc are algae species widely used in cosmetology due to the pigments: a-chlorophyll and b-chlorophyll [4].

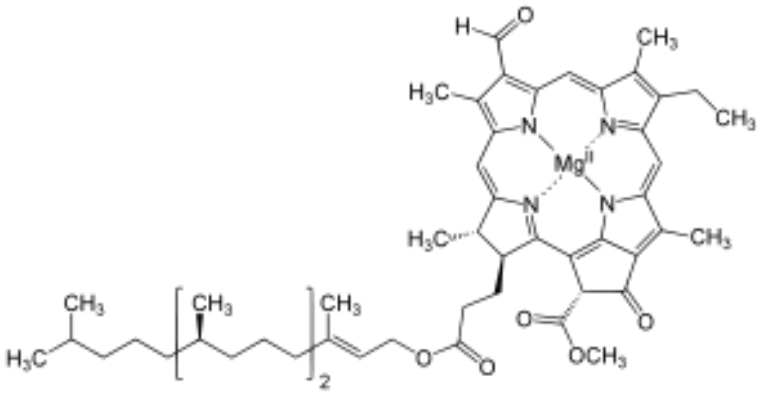

Figure 3. Structural formula of the chlorophyll compound

b-Chlorophyll (Figure 3) is structurally similar to a-chlorophyll, just as a-chlorophyll participates in the process of photosynthesis. b-Chlorophyll absorbs energy while a-chlorophyll does not. Chlorophyll is found in Spirulina spp. which, in addition to pigments and fatty acids, also contains vitamins and minerals that are widely used in cosmetology [8]. It has antioxidant, anti-inflammatory, anti-wrinkle effects, gives elasticity to the skin as well as participates in collagen synthesis and moisturizing [5, 6]. Due to its ability to inhibit odors, chlorophyll is used in the production of deodorants and toothpaste [10].

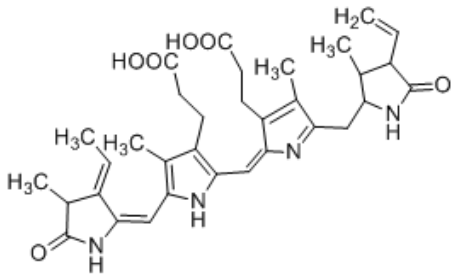

Figure 4. Structural formula of the phycoerythrin compound

Phycoerythrin (Figure 4), the red pigment responsible for the photosynthesis process, reflects red light and absorbs the blue one [4]. It is responsible for capturing light from

the red to green spectrum of light. According to its absorption spectrum, phycoerythrin can be divided into three classes: β-phycoerythrin (545–565nm), R-phycoerythrin (499–565nm) and C-phycoerythrin (565nm) [13]. From a structural point of view, it is composed of the chromatophores contained in phycobilins. Phycoerythrin pigment possesses anti-inflammatory, moisturizing, nourishing and soothing properties on the skin as well as an emollient [5, 6]. This pigment is found in the algae from the species of the Porphyridium genus, as well as in cyanobacteria [8, 11] which, in addition to their biologically active properties, are considered to be an alternative to artificial dyes. Following the biotechnological process, this pigment serves as a base for lipsticks and eye pencils. [8] Obtaining cosmetic products based on phycobiliproteins (PBPs) is very expensive due to a low extraction yield and chemical instability. Also, these compounds tend to suffer denaturation in light and heat. Due to the fact that the production of PBP from natural sources requires a large investment in the cultivation of cyanobacteria, cultivators for the mass production of cyanobacteria and algae on a large scale are now being created.[10]

3. Conclusions

According to the previously described review and the subsequent development of cosmetology, pharmacists rely on the development of new biological technologies for obtaining useful pigments for various branches. Synthetic compounds in cosmetology often produce adverse effects, while the natural ones, extracted from algae or cyanobacteria, are hypoallergenic, antioxidant, anti-melanogenic, anti-cancer, anti-aging, antimicrobial and anti-inflammatory. So the development of biotechnology is promising both for cosmetology and for other branches of the industry.

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Structure of edaphic algoflora on agricultural land cultivated with vineyards and orchards in the southern districts of the Republic of Moldova

Eugeniu Ciobanu

Abstract. This article addresses the problem related to edaphic algoflora characteristic of vineyards and orchards in the southern districts of the Republic of Moldova. On the basis of the taxonomic structure of some dominant species of algae we can determine the accumulation capacity of nutrients in the soil and, respectively, fertility, due to the fact that algae, due to the metabolic processes, eliminate in the environment a number of bioactive substances, which stimulate the development of crop plants. Thus, the study of edaphic algoflora on agricultural lands is of great interest for Agriculture.
Keywords: edaphic algae, algoflora, phylum, class, fertility.

Structura algoflorei edafice pe terenuri agricole cultivate cu vii și livezi din raioanele de sud ale Republicii Moldova

Rezumat. În articolul dat este abordată problema ce ține de algoflora edafică caracteristică viilor și livezilor din raioanele de sud ale Republii Moldova. În baza structurii taxonomice a unor specii dominante de alge putem determina capacitatea de acumulare a elementelor nutritive din sol și respectiv fertilitatea, datorită faptului că algele în urma proceselor metabolice eleimină în mediul înconjorător un șir de substanțe bioactive, care stimulează dezvoltarea plantelor de cultură. Astfel, studierea algoflorei edafice de pe terenurile agricole prezintă un interes mare pentru agricultură.
Cuvinte cheie: alge edafice, algoflură, filum, clasă, fertilitate.

1. Introduction

Algae represent a good part of the edaphic microorganisms that multilaterally influence different processes occurring in soil, contributing directly or indirectly to the modification of its physicochemical properties [1].

A very important partcularity of the soil biota is represented by edaphic algae, being some of the most representative indicator organizations of the environmental state. Based on the taxonomic structure and the number of dominant species, we can appreciate the soil ability to naturally accumulate nutrients that makes it possible to determine soil fertility [2]. Algae also play a special role in soil self-cleaning, rain prevention and wind

erosion [3]. Some cyanobacteria have the ability to fix atmospheric nitrogen in the soil, mobilize many chemical elements, depolute soils polluted with herbicides, insecticides, etc., thus contributing to the increase of crops [8]. In addition, algae that do not have the capacity to fix atmospheric nitrogen include in their biomass an important amount of biologically active substances which, after the decomposition of algal biomass, get into the soil and play an important role in the efficient development of pedogenetic processes with a stimulating effect on vegetation [4].

The development and spread of algae in soils depends not only on climatic factors such as temperature, humidity, lighting level, etc.and the work done on it. Rational soil processing increases its fertility and activates biological processes, contributing to the creation of favorable conditions for the entire soil biota [6]. Selectively absorbing salts, algae contribute to the biogenic distribution of elements in the soil [5].

According to literature data, the role of algae in the soil formation process is more commonly analyzed at the early stages of pedogenesis. Thus, algae are assigned the role of the main source of organic matter necessary for microbial functioning. The latest research has shown that along with the pedogenetic evolution of soil, the role of algae in it also increases. Thus, the direct participation of algae in the biochemical and physical processes in soil was demonstrated as: accumulation of organic substances and fixation of atmospheric nitrogen, primary and secondary decomposition of minerals and accumulation of biophilic elements and aggregates[11].

In the process of soil recultivation there is an increase in the number and diversity of bacteria, actinomycetes and other organisms as well as edaphic algae in the soil. At the same time, other physicochemical processes caused by algae are established, such as their contribution to the modification of gas and water regimes in the soil [6].

2. Materials and methods

Research in the field of algae distribution in different soil types occupied with various agricultural crops was carried out based on soil samples collected from Cimişlia district. The collection of samples and their analysis was carried out according to the methods widely applied in edaphic Algology. The analyzed soil samples represent a mixed soil sample consisting of 10 individual samples with a volume of 5 cm^3 each, collected from an area equal to 100 m^2. The distance between individual samples was not less than 5 m. The collected soil was stored in a pre-sterilized “Craft” hard paper package, after which they were transported to the laboratory and inoculated in Petri dishes with glass blades, where in the laboratory conditions were created for the growth and development of algae from the samples under study[7;9]. The species were determined according to

derminators "Определитель пресноводных водорослей" вып. 1-14; "Визначник прісноводных водоростей УССР" (1968б 1976б 1979б 1984); " Определитель протококковых водорослей Средней Азии" (1979а,б); В. М. Андреева " Род Chlorella" (1975) A. Pascher "Die Susswaserflora Deutschlands", Osterreichs und der Schweiz (1914, 1915, 1925); H. Ettl "Susswasserflora von Mitteleuropa" (1978); K. Starmach "Flora sladkovodna Polski" (1963, 1966, 1968, 1971); H. Skuja "Taxonomiedes phytoplanctons einige Seen in Uppland, Schweden" (1948); F Hindak "Studies the chlorococcal alga (Chlorococcophyceae)" (1980, 1984, 1988);.... Bold "Phycological studies" The university of Texas publication v. 5, v.6, v.7, v.8, v.9, v.10, v.11 (1964, 1966 a,b, 1969 a,b, 1970a,b.

3. Results and discussion

The investigations carried out open up great perspectives for the use of edaphic algae as biological indicators of the state of soil, in part, and of the environment, in whole [10]. The information regarding the peculiarities of distribution and formation of algal communities depending on the nature of biological and ecological peculiarities of crop plants allows us with a higher probability to assume the presence of certain species of algae in these soils. This greatly facilitates the process of selecting some strains of algae as biotechnological objects.

As a result of the research of soil samples collected from the orchards in Cimişlia Ciucur Minjir village there were highlighted 83 species and varieties of algae that refer to 37 genera, 23 families, 9 orders that refer to four phylums: Cyanophyta – 33, Xanthophyta – 23, Chlorophyta – 21, Bacillariophyta – 6 (tab. 1; fig 1).

Table 1. Taxonomic structure of edaphic algae communities in the soils occupied with orchards

Phylum	Cyanophyta	Xanthophyta	Chlorophyta	Bacillariophyta	Total
Order	2	3	3	1	9
Families	5	7	8	3	23
Generas	9	13	12	3	37
Species	33	23	21	6	83

Following the analysis of soil samples collected from the areas occupied by vineyards in Cimislia Ciucur Minjir village, 42 species and varieties of edaphic algae from 25 genera, 18 families and 9 orders referring to four phylums were highlighted: Cyanophyta – 10, Xanthophyta – 16, Chlorophyta – 13, Bacillariophyta – 3 (tab. 2; fig. 2).

Table 2. Taxonomic structure of edaphic algae communities in soils occupied with vineyards

Phylum	Cyanophyta	Xanthophyta	Chlorophyta	Bacillariophyta	Total
Order	2	3	3	1	9
Families	3	7	6	2	18
Generas	5	10	8	2	25
Species	10	16	13	3	42

Following the analysis of the data obtained from the samples collected in the fields occupied by orchards, 83 species of algae were identified, of which cyanophytes - 33, xanthophytes - 23, chlorophytes - 21, bacillariophytes - 6. It has been established that the dominant species belong to the first three phylums. They actively participate in the process of pedogenesis, as well as nitrogen fixation and accumulation of microelements in the soil.

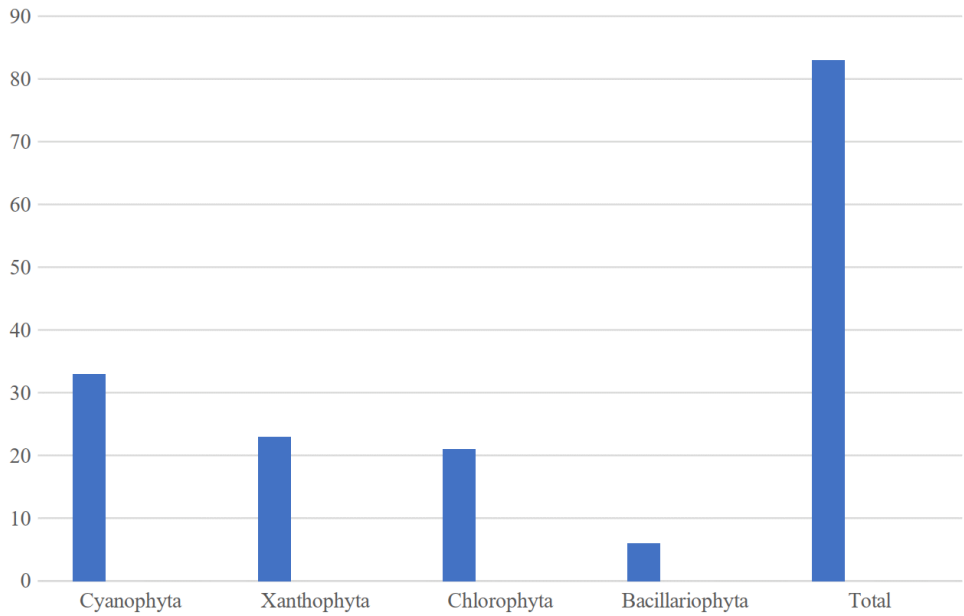

Figure 1. Numerical distribution of edaphic algae species in the ecosystem planted with orchards

The most abundant species of those identified are: *Nostoc pruniforme Born. et Flah., Anabaena variabilis Kütz., Oscillatoria brevis Kütz. ex Gom. Phormidium ambiguum Gom. ex Gom., Phormidium tenue (Ag. ex Gom.) Anagn. et Kom., Nostoc commune*

f. sphaericum (Vauch.) Elenk., Gloeocapsa magma (Bréb.) Kütz., *Phormidium terebriforme (Ag. ex Gom.) Anagn. et Kom., Oscillatoria chalybea Mert. ex Gom.* from cyanophytes, *Chlorococcum infusionum (Schrank) Menegh* from chlorophytes , *Chloridella feruginosum Pasch* from xantophytes *Hantzschia amphioxys (Ehrb.) Grun. in Cl. et Grun.* from bacillariophytes.

The fields cultivated with vineyards are very poor in algae species, here being identified only 42 species of which cyanophytes - 10, xanthophytes - 16, chlorophytes - 13, bacillariophytes-3; dominant being those of the first three phylums.

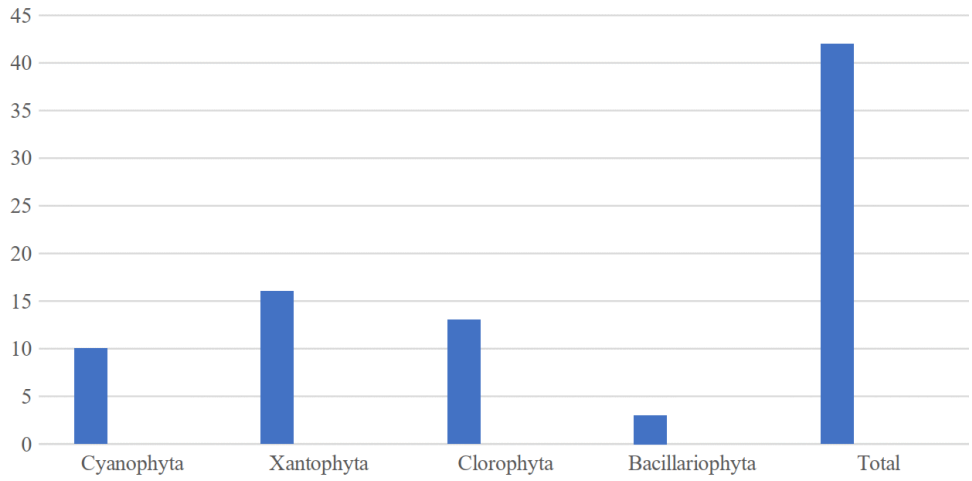

Figure 2. Numerical distribution of edaphic algae species in the ecosystem planted with vineyards

The most frequently encountered species of those identified are: *Phormidium ambiguum, Phormidium tenue, Gleocapsa minor, Gleocapsa magma* from cyanophytes, *Chloorococum infusionum, Chloorococum gelatinosum* from chlorophytes, *Chloridella feruginosum, Chloridella simplex Pasch* from chlorophytes, *Hantzschia amphioxis* from bacillariophytes.

4. Conclusions

Generalizing the presented data, we can identify the taxonomic structure of edaphic algoflora and the principles of algoflora formation in vineyards and orchards. Analyzing the data from Table 1 and Table 2, we identify four dominant phylums: Cyanophyta, Xanthophyta, Chlorophyta and Bacillariophyta of which the most numerous are the algae from the first three phylums. However, the results show a smaller number of species

compared to the cultivated lands with annual or biennial crops due to the specific conditions that are formed in these habitats. On the fields cultivated with vineyards algoflora is very poor due to their processing with copper sulfate (bordolese juice) which also has a negative effect on algae. However, we can identify genera and species of algae that are specific to vineyards and orchards, and may have application in biotechnology.

The study was carried out within the scientific research project "development of new multifunctional materials and efficient technologies for agriculture, medicine, technology and education system based on metal complexes "s" and "d" with polydentate ligands", included in the "state Program" (2020-2023) - 20.80009.5007.28.

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DFT study of condensation mechanisms of 4-pyridinecarboxaldehyde with o-, m-, p-aminobenzoic acids

Ion Arsene, Eduard Coropceanu, and Viorica Purcel

Abstract. It was theoretically studied the mechanism of the condensation reaction of 4-pyridinecarboxaldehyde with o-, m- and p-aminobenzoic acids. Theoretical calculations represent a primary advantage in studying these reactions, along with the determination of a wide range of molecular properties. The studied reactions take place in two stages, each stage is accompanied by a transition state and for each stage it is calculated the activation energy. Thermodynamically speaking, all reactions are endothermic and the most convenient from an energetic point of view is the reaction for obtaining 4-(pyridine-3-yl-methylene amino) benzoic acid in methanol with an energy value of 9.98 kcal/mol.

Keywords: mechanism, DFT calculations, Schiff bases, energetic stability, transition state.

Studiul DFT al mecanismului de condensare a 4-piridincarboxaldehidei cu acizii o-, m-, p-aminobenzoic

Rezumat. A fost studiat teoretic mecanismul reacției de condensare a 4-piridincarboxaldehidei cu acizii o-, m- și p-aminobenzoici. Calculele teoretice reprezintă un avantaj primordial în studierea acestor reacții, cu determinarea a unei game largi de proprietăți moleculare. Reacțiile studiate decurg în două etape, fiecare etapă este însoțită de câte o stare de tranziție și pentru fiecare etapă calculându-se energia de activare. Termodinamic vorbind, toate reacțiile sunt endoterme și cea mai convenabilă din punct de vedere energetic este reacția de obținere a acidul 4-(piridin-3-il-metilenamino)benzoic în metanol cu valoarea energiei de 9,98 kcal/mol.

Cuvinte cheie: mecanism, calcule DFT, baze Schiff, stabilitatea energetică, stare de tranziție.

1. Introduction

Current chemical engineering has the task of developing new chemical compounds that would allow obtaining materials with useful properties for various fields. A rapidly developing field at the intersection of inorganic and organic chemistry is coordination chemistry, which offers effective solutions for various fields: agriculture, industry, pharmaceuticals

etc. [1]. One of the most important components in the synthesis of coordination compounds is coordination agents (ligands), the nature of which can radically influence the structure and properties of new metal-organic molecules.

Schiff Bases present valuable coordination agents in the synthesis of coordination compounds, which allow diversification of the composition and structure of the final products. The geometric peculiarities of organic molecule, the presence of electron-donating atoms, as well as the nature of metal ions generating the complex, create the prerequisites for the assembly of new molecular architectures with distinct properties. To obtain organic molecules that would have a greater interest in the coordination process, precursors are used that would ensure the presence of various functional groups: pyridinic, carboxylic etc. [2].

The compounds obtained from the condensation which contain a pyridinic nucleus possess a series of pharmacological properties, being described in the literature as antimicrobial [3], anti-inflammatory [4], antioxidant [5], etc. There are a variety of mechanisms by which condensation occurs and this depends on the chemical nature of the reactant groups and the environment in which the reaction occurs (temperature, presence of catalysts, the solvent used etc.).

Condensation of different organic molecules and obtaining Schiff bases allowed the synthesis of coordination compounds with a special composition and molecular architecture, which manifest various useful properties such as luminescence, absorption of small molecules etc. [6-9]. The theoretical study of Schiff bases with tautomeric forms was previously carried out in a series of papers [10, 11]. Theoretically, the mechanism of the condensation reaction was studied in the papers [12, 13] where the general mechanism and energy profile of the reactions are described. The thermodynamic parameters are also studied with the estimation of thermal effect values.

Different solvents can influence the equilibrium constant of a reaction by stabilizing the reactant or product. The equilibrium is shifted in the direction of the substance that is preferably stabilized. Stabilization of the reactant or product can occur through various non-covalent interactions with the solvent, such as hydrogen bonding, dipole-dipole interactions and Van der Waals interactions [14].

In this research, the condensation mechanisms of 4-pyridinecarboxaldehyde with o-, m-, and p-aminobenzoic acids will be studied, studying the influence of the solvent on the energy profile of the reaction.

2. Computational methods

The optimization of the geometric structures of the species participating in the condensation reaction was calculated, using the Density Functional Theory (DFT) with the hybrid exchange-correlation functional B3LYP (Becke with the functional correlation of three parameters: Lee, Yang, and Parr), and the standard basis set 6-31G [15, 16], using the GAUSSIAN 09 program. Through the IRC method, the configurations of reactants and reaction products were obtained, as well as the analysis of intrinsic reaction coordinates was performed to confirm the connectivity between the transition state and a local minimum [17].

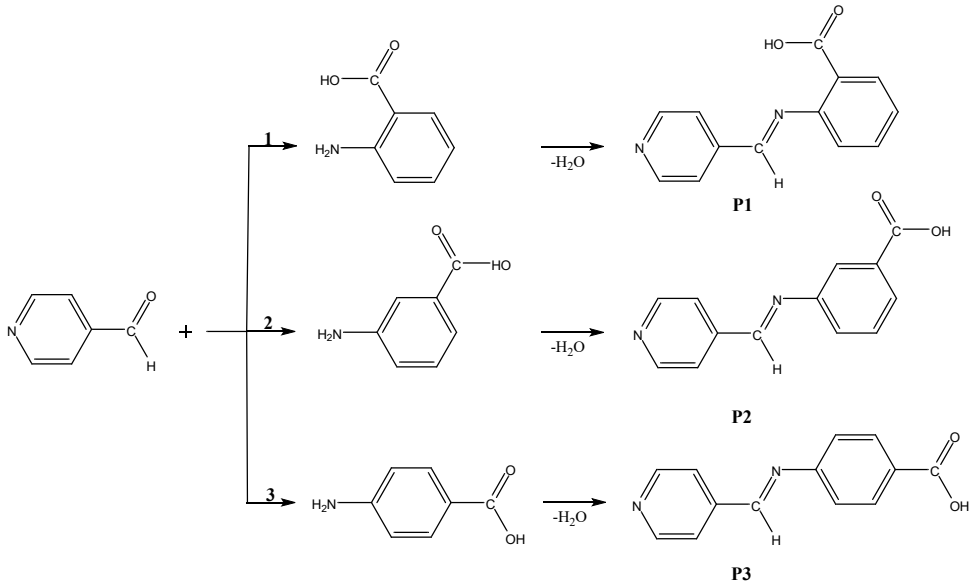

Figure 1. The general mechanism of condensation of 4-pyridinecarboxaldehyde with o-, m-, p-aminobenzoic acids

3. Results and discussion

As part of the research, theoretical studies of the mechanisms of condensation reactions of 4-pyridinecarboxaldehyde with o-, m-, and p-aminobenzoic acids were carried out both in a vacuum and in solvent (methanol). There was studied the mode of interaction of the ligands, in particular, and obtaining three Schiff bases: 4-(pyridine-2-yl-methylene amino) benzoic acid (**P1**), 4-(pyridine-3-yl-methylene amino) benzoic acid (**P2**) and 4-(pyridine-4-yl-methylene amino) benzoic acid (**P3**). The geometric and energetic parameters (stabilization energy, activation energy, caloric effect) of the condensation reactions were also studied.

Theoretical study of the interaction of 4-pyridinecarboxaldehyde with o-aminobenzoic acid. The first reaction studied is the interaction of o-aminobenzoic acid with 4-pyridine carboxaldehyde, as a result of which 4-(pyridine-2-yl-methylene amino) benzoic acid was obtained (Figure 1, **P1**). According to the general scheme in Figure 1, the mechanism of the condensation reaction with the formation of 4-(pyridine-2-yl-methylene amino) benzoic acid shown in Figure 2 was elaborated.

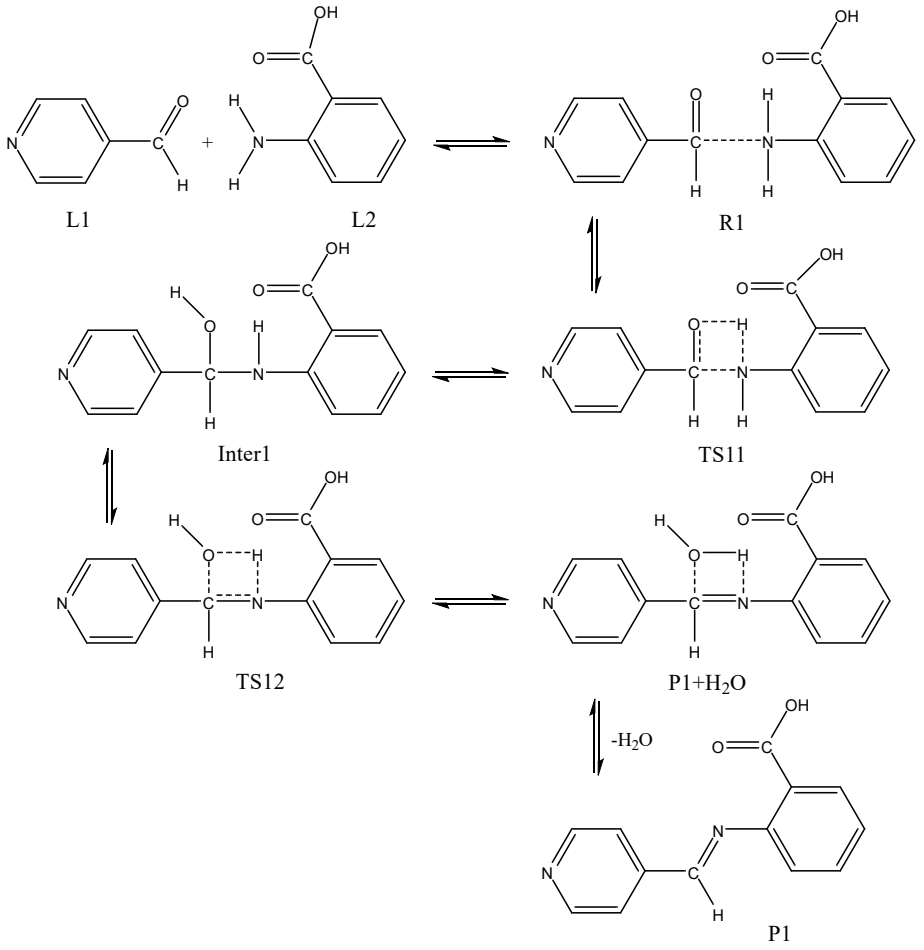

Figure 2. Mechanism of the reaction to obtain the 4-(pyridine-2-yl-methylene amino) benzoic acid (**P1**)

Studying this stage, both in a vacuum and in a solvent, a transition state (**TS11**) is obtained, with the value of the activation energy, respectively, equal to 46.31 kcal/mol and 43.62 kcal/mol and a single imaginary frequency of -1564.43 cm^{-1} and 1569.41 cm^{-1} (Figure 3).

In the second step, the intramolecular transfer of the second hydrogen atom from the group ($–NH_2$) to the oxygen atom of the group (–OH) takes place. As a result, a water molecule is eliminated, obtaining the final compound (**P1**) which is energetically stable. This step is accompanied by a transition state (**TS12**) with the value of the reaction barrier in a vacuum and solvent, respectively, equal to 56.66 kcal/mol and 54.91 kcal/mol and imaginary frequencies of -1778.92 cm^{-1} and -1785.32 cm^{-1} (Figure 3).

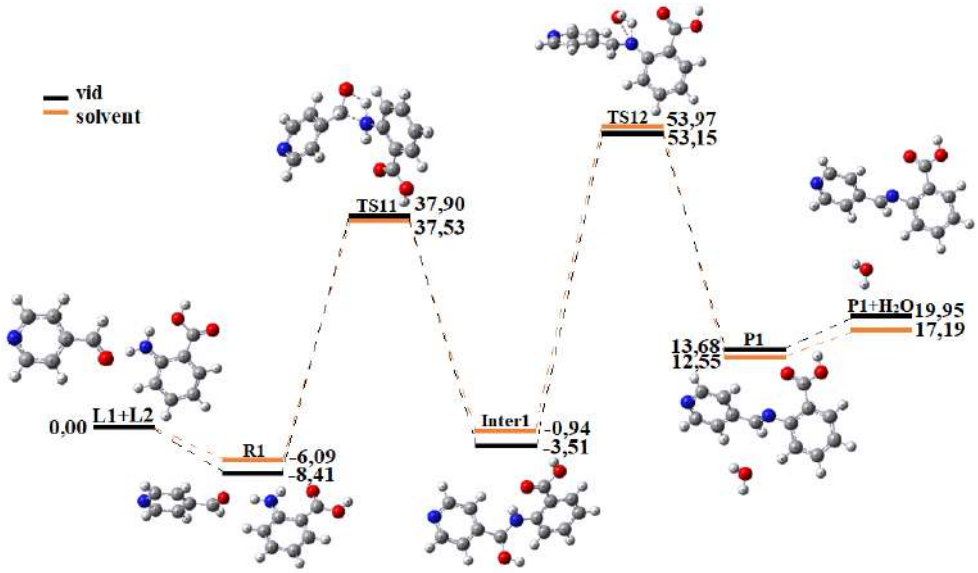

Figure 3. Energy profile of the condensation reaction between 4-pyridinecarboxaldehyde and o-aminobenzoic acid expressed in kcal/mol

Analyzing the structure of the species participating in the first stage of the reaction and their energetic stability, and taking into account the reaction environment, energetically speaking, the reaction barrier in the case of the solvent is lower than in the vacuum one by 2.69 kcal/mol, which shows us that the reaction proceeds more easily in the solvent. We can also conclude that from a thermodynamic point of view, the most energetically favorable reaction is the one that takes place in the solvent, with a gain of 2.76 kcal/mol.

Theoretical study of the interaction of 4-pyridinecarboxaldehyde with m-aminobenzoic acid. The interaction of 4-pyridinecarboxaldehyde with m-aminobenzoic acid was studied, obtaining a new organic product – 4-(pyridine-3-yl-methylene amino) benzoic acid (Figure 1, **P2**). According to Figure 1, the mechanism of condensation reaction was elaborated (Figure 4), with the formation of 4-(pyridine-3-yl-methylene amino) benzoic acid (**P2**) as the final product.

In the first stage of this reaction, the interaction of 4-pyridinecarboxaldehyde with m-aminobenzoic acid takes place according to the mechanism of the condensation reaction (Figure 1, **P2**). Following this interaction, the intermolecular transfer of a hydrogen atom from the amine functional group ($–NH_2$) to the oxygen atom in the aldehyde group (–CHO) takes place, obtaining a relatively stable intermediate compound (**Inter2**).

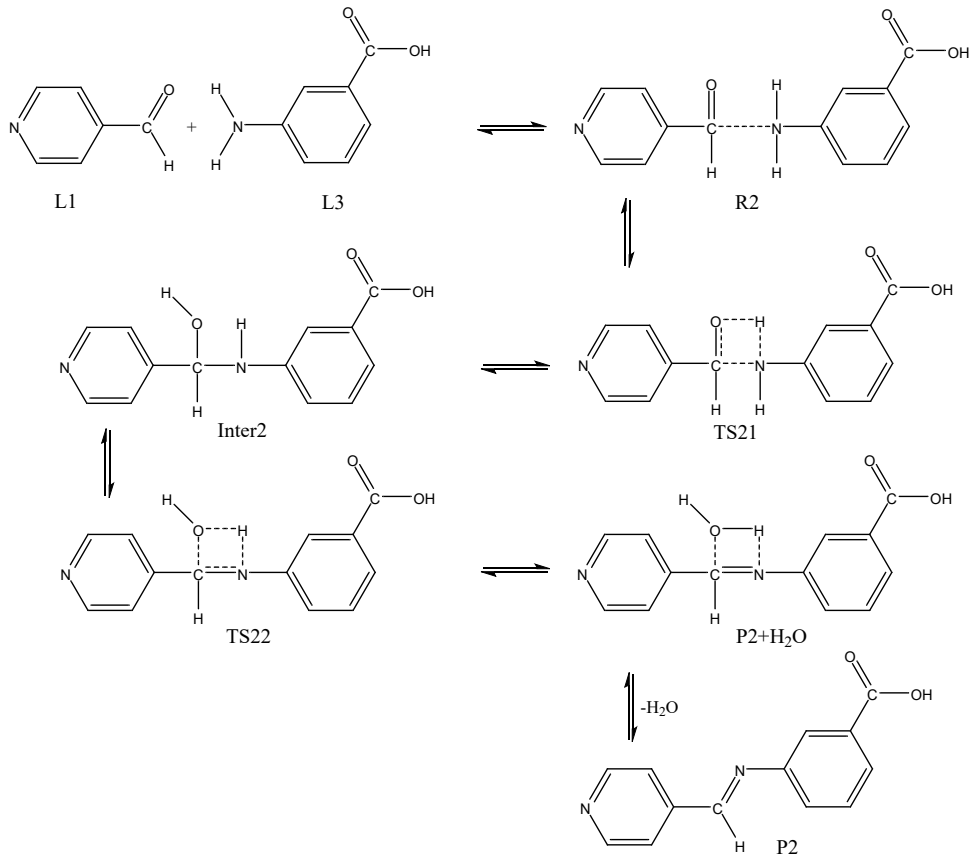

Figure 4. Mechanism of the reaction to obtain the 4-(pyridine-3-yl-methylene amino) benzoic acid (**P2**)

The transition state (**TS21**) at this stage was identified because it has a unique imaginary frequency: -1602.17 cm^{-1} and -1565.04 cm^{-1} in vacuum and solvent, respectively. The value of reaction barrier in vacuum and solvent is equal to 44.18 kcal/mol and 40.01 kcal/mol, respectively. On the basis of the energies obtained, the total energy profile of the condensation reaction was built (Figure 5).

The second step proceeds with the transfer of the second hydrogen atom from the group ($–NH_2$) to the group (–OH). Also, the elimination of a water molecule takes place and the

final compound (**P2**) is energetically stable 4-(pyridine-3-yl-methylene amino) benzoic acid.

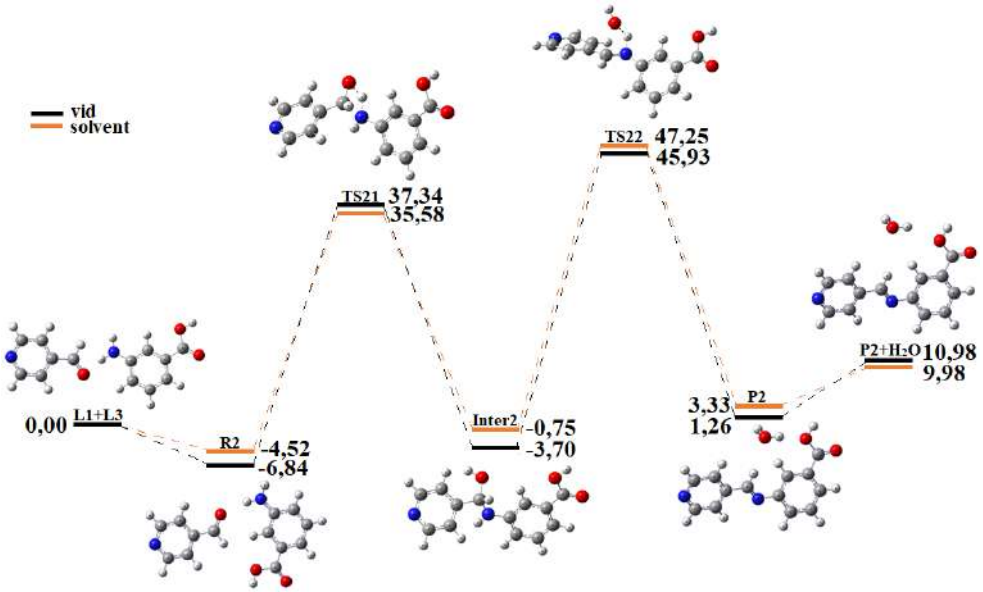

Figure 5. Energy profile of the condensation reaction of 4-pyridinecarboxaldehyde m-aminobenzoic acid expressed in kcal/mol

Analyzing the energetic stability, structure of the species participating in the reaction and taking into account the reaction environment, from the energetic point of view, the activation energy in the case of the solvent at the first stage, is lower than vacuum by 4.08 kcal/mol. Thus, the positive effect was demonstrated of the solvent on the reaction. From a thermodynamic point of view, the most energetically favorable reaction takes place in the solvent, with a gain of 1.0 kcal/mol.

Theoretical study of the interaction of 4-pyridinecarboxaldehyde with p-aminobenzoic acid. The theoretical study of the interaction of 4-pyridinecarboxaldehyde with p-aminobenzoic acid was carried out both in vacuum and solvent (methanol), obtaining a new organic product – 4-(pyridine-4-yl-methylene amino) benzoic acid (Figure 1, **P3**) [18]. The general scheme of the condensation reaction mechanism is shown in Figure 1. For all species participating in the reaction, the geometric structure was determined with the calculation of geometric and energetic parameters, which are comparable to those in the specialized literature.

According to the developed mechanism of the reaction represented in Figure 6, the reaction proceeds in two stages. First of all, the interaction of a molecule of

4-pyridinecarboxaldehyde with p-aminobenzoic acid takes place according to the mechanism of the condensation reaction. As a result of the interaction, the intermolecular transfer of a hydrogen atom from the amine functional group (–NH_2) to the oxygen atom in the aldehyde group (–CHO) takes place, forming a new intermediate compound (**Inter3**).

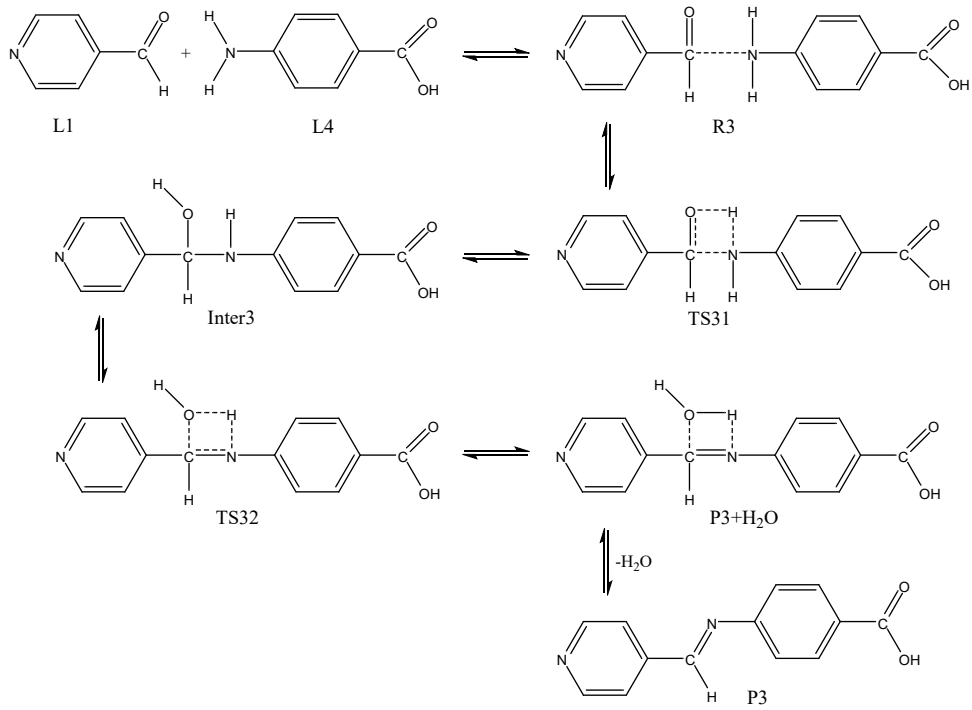

Figure 6. Mechanism of the reaction to obtain the 4-(pyridine-4-yl-methylene-amino) benzoic acid (**P3**)

The first step is accompanied by a transition state (**TS31**), with the value of the reaction barrier in vacuum and solvent, respectively equal to 45.74 kcal/mol and 43.68 kcal/mol, and the imaginary frequencies: -1609.4 cm^{-1} and -1573.12 cm^{-1}, respectively in vacuum and solvent.

In the second step, the transfer of the second hydrogen atom from the (–NH_2) group to the (–OH) group takes place. This way a water molecule is removed and it is obtained the final compound (**P3**) stable from the energetic point of view.

Analyzing the energy scheme in Figure 7, the reaction barrier in the case of the solvent in the first step is lower than in a vacuum by 2.06 kcal/mol, which shows that the solvent favours the faster course of the reaction.

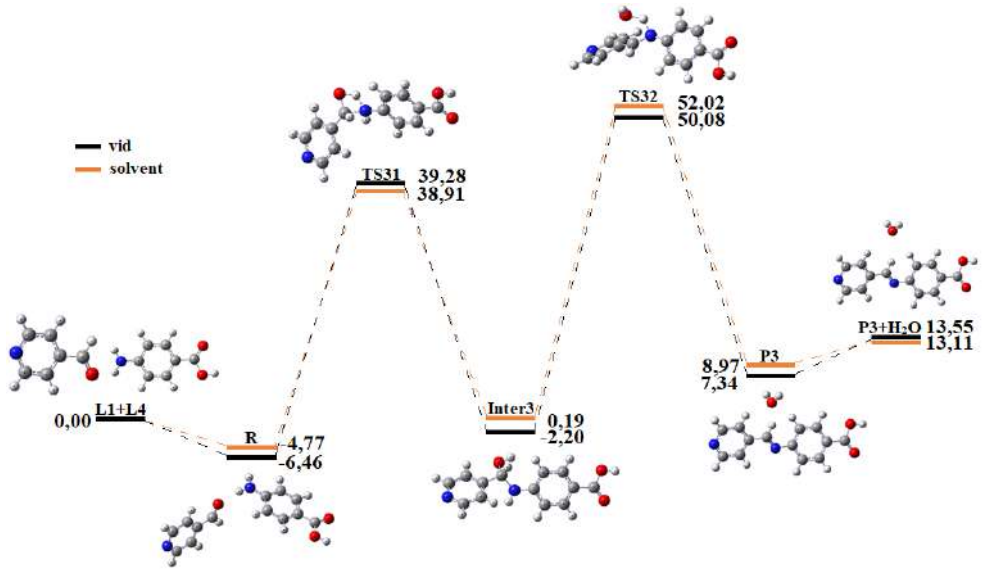

Figure 7. Energy profile of the condensation reaction of 4-pyridinecarboxaldehyde with p-aminobenzoic acid expressed in kcal/mol

Analyzing the structure of the species participating in the reaction and their energetic stability, and taking into account the reaction environment, it can be concluded with certainty that the most energetically convenient reaction is the one that takes place in solvent, with a gain of 0.44 kcal/mol.

The study carried out allows the formulation of conclusions about the energetics of the condensation process of 4-pyridinecarboxaldehyde o-/m-/p-aminobenzoic acid in the perspective of using the reaction products as coordinating agents for the assembly of new coordinating compounds with various properties. In turn, the coordination process is of interest from the point of view of the coordination of the functional groups of the new organic compound to various metal ions.

4. Conclusions

Quanto-chemical calculations are a theoretical way to determine the probability of a reaction occurence, anticipating some processes and applying them practically, we can obtain synthetically new compounds of high purity, saving time and reagents needed for a possible repetition of the condensation process in case there was not obtained the expected product. The mechanisms of the condensation process of 4-pyridinecarboxaldehyde with o-, m- and p-aminobenzoic acids in vacuum and solvent (methyl) were developed where

the solvent favours the faster course of the reaction, having lower activation energy compared to the vacuum one.

All the studied reactions take place in two stages and each stage is accompanied by a transition state. It should be noted that in the first stage the activation energy for the o-, m-, and p- reactions are respectively equal to 46.31, 44.18 and 45.74 kcal/mol, indicating higher values compared to the activation energy of the reaction in methanol – 56.66, 49.63 and 52.78 kcal/mol.

Studying these reactions thermodynamically, we can state that all reactions are endothermic and the most convenient from an energetic point of view is the reaction to obtain 4-(pyridine-3-yl-methylene amino) benzoic acid in methanol with an energy value of 9.98 kcal/mol.

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Pavel Pulbere - promoter of Biology teaching in the Republic of Moldova

Lora Moshanu-Shupac and Nina Liogchii

Abstract. The paper is dedicated to the 25th anniversary of the death of Professor Pavel Ion Pulbere, PhD in Biological Sciences, Tiraspol State University.
Keywords: biographical files, didactic and scientific activity, managerial activity.

Pavel Pulbere - promotor al didacticii Biologiei în Republica Moldova

Rezumat. Lucrarea este consacrată celei de-a 25-a aniversări de la trecerea în neființă a profesorului Pavel Ion Pulbere, doctor în științe biologice, Universitatea de Stat din Tiraspol.
Cuvinte cheie: file biografice, activitatea didactico-științifică, activitate managerială.

Portrait of Professor Pavel Pulbere. A combination of physical and intellectual stature, gentle, penetrating gaze, upright social posture, with a prosocial behaviour, respectful towards people, with a great work capacity, huge creative potential, profound knowledge in his speciality work field and an exceptional gift of transmitting it - **this is the portrait of Professor Pavel Pulbere**.

Figure 1. Pulbere Pavel Ion, PhD in biological sciences, associate professor (1935-1997)

1. Biographical files

Pulbere Pavel Ion was born on August 2, 1935 in Gaspar village, Edinet district in a peasant family. In 1953 he graduated from the secondary school in Parcova village, then he studied at the Faculty of Biology and Chemistry of the Pedagogical Institute in Balti for one year. In 1954-1957 he continued his studies in the same field at the Pedagogical Institute in Tiraspol and graduated with honours as ***a school teacher of Biology and Chemistry***.

In 1957 he began his pedagogical activity at the middle school in Telenesti. In August 1958 he was elected secretary of the district committee of Telenesti county, a position he held for a year.

In 1959 he moved to the State Pedagogical Institute in Tiraspol as assistant to the Department of Zoology. In 1962 he was elected senior lecturer of the same department and Dean of the Faculty of Natural and Geographical Sciences, a position he held until October 1964 (1,4).

In parallel to his teaching activity he was also interested in research. In 1960 he published this first scientific work devoted to the study of the influence of cholinesterase on experimental atherosclerosis, and in 1962 he initiated a brilliant series of experimental investigations of the influence of central nervous system on the metabolism of cholesterol. On the basis of this research he developed a new method of modelling experimental atherosclerosis and revealed the role of biologically active substances of natural origin in the regulation of cholesterin metabolism.

From September 1, 1966 Pavel Pulbere continued his research at the Institute of Medicine in Leningrad (Russia, now Saint Petersburg) for doctor's training and the obtained scientific results were the basis for his PhD thesis in Biology in 1967 on "Influence of the functional state of the central nervous system on the cholesterin metabolism and experimental atherosclerosis" (5).

Returning to the faculty, in 1968 he was appointed as interim university lecturer in the Department of Human and Animal Physiology, and in 1971 the Higher Certification Commission awarded him the scientific and teaching title of associate professor. For many years Mr. Pulbere was a member and president of the Republican School Olympic Committee in Biology, he headed the Commission for awarding teacher degrees to Biology teachers in the republic. In 1970 he was awarded the badge "Eminent in public education" for outstanding achievements in the field of teaching and science and in 1981 - the badge for "Eminent achievements in activity" (4).

Due to his remarkable leadership skills he held various leading positions, such as Dean of the Dean of the Faculty of Biology and Chemistry (1969-1978), Head of the Department of Human and Animal Physiology (1977-1992) and in parallel – Vice Rector for Didactic Activities (1983-1988).

Due to the national political events in 1992, together with the University staff, Mr. Pulbere fled to Chisinau. In addition to his teaching activity at the Department of Human Physiology, he held the position of Dean of the Faculty of Biology and Chemistry until 1996 when his health began to deteriorate.

Figure 2. Laboratory work in Human Physiology guided by Mr. Pavel Pulbere

2. Didactic and scientific activity

During his managerial activity Pavel Pulbere has shown perseverance with himself and his subordinates, discipline, responsibility in successful accomplishment of his tasks; and has always considered being a teacher as his main mission. He made considerable efforts to organize the teaching process and scientific work, participated in the development of the concept of pedagogical training by providing teachers with methodical teaching materials and developed the experimental side of biological sciences, thus emphasized learning through exploration. The following pictures show him among students.

In the course of his scientific and pedagogical activity he published about 60 scientific and methodical papers devoted to the problem of increased excitability of the central nervous system during the development of experimental atherosclerosis in animals. Having a vast experience and being a teacher by vocation, he devoted a good part of his works to methods of teaching Biology in higher and secondary education. For his prodigious work Mr. Pulbere has been awarded many times with diplomas of mention by the Ministry of Education. In over 40 years of activity in Tiraspol State University he has contributed to the pedagogical training of more than 20.000 specialists in the fields of Biology, Chemistry, Geography and Pedagogy. Thanks to his erudition, his oratorical skills and his high standards of education, he saw in each student a unique personality and did not diminish their human aspect. He was determined to cultivate their love for books (5). The memory of the famous and distinguished pedagogue and scientist has been preserved by the creation of the laboratory in his name at the Faculty of Biology and Chemistry where students have the opportunity to carry out laboratory work and research studies in the framework of their bachelor and master theses.

3. The teacher lives through his disciples

Being the disciples of professor P. Pulbere, today and forever we will fondly browse through the memories that link us to his personality.

Through these deeply sincere lines, we will try to set the example of Professor Pavel Pulbere to those young university students of today and tomorrow, to those who did not know him and who do not know that they are and will be for a long time to come students of Professor Pulbere. This is confirmed by the fact that Mr. Pulbere's name is recognised by his disciples, is respected by our country's teachers, his colleagues and all those who have had the priviledge of knowing him.

Professor Pavel Pulbere has trained and inspired generations of teachers and scholars who keep the light burning. He was the person who was at the start of the teaching and scientific careers of many students, handing them the admission card. Further on sharing with them his rich treasure of knowledge and qualities. Which facilitated them to successfully graduate in five years and teach in schools all around the country. While other of his graduates enjoyed the opportunity to work at the Department of Human Physiology of the Faculty of Biology and Chemistry of Tiraspol State University, or in other scientific and higher national education institutions.

Being an intelligent and warm-hearted person, he interacted with his disciples not only during lessons, but also in various other situations, showing great esteem towards them and helping them to solve problems that they were facing. He was always interested in student life and did not hesitate to visit them in the dormitory, at the college, at evening events organised on different occasions. On New Year's Eve he used to come with heartfelt congratulatory messages and join the student hora. He had his own way of being, putting a lot of heart and effort into conveying his experience through his gift of informing and persuading. Every lesson was a lesson of life. His unique way of asking questions, raised an avid interest in finding out the scientific truth. This challenge led the students slowly down the path of knowledge (2).

Now, after the passing of many years of professional and human training of his disciples, after the former students have gained a great deal of life experience, they can say with certainty that there is no teacher who has not enlightened their souls. We say this because all the teachers who taught and educated us, from the first day of school to the last day of university, and even more so the last day of the doctorate, have remained in our memory forever. Memories bring us back more and more often to the times when we were with them, to their gentle faces, their calm voices, and we marvel at the grace and skill with which they took us into the world of pedagogy and biological sciences. Among

the brightest and most vivid faces that often appear is that of Pavel Pulbere, Doctor of Biological Sciences, Associate Professor, whom we, former students, have known since the first year at the Faculty of Biology and Chemistry of the State Pedagogical Institute "T.G.Shevchenko" in Tiraspol. Even then, the hearts and souls of many students felt the kindness of this great teacher. A personality who was the starting point in their professional activity, a pedagogue who enormously contributed to their professional and managerial training, and who trusted them and inspired trust along the way (3).

His strong temperament, generosity, desire to support and do good, modesty, rigour and principledness made him a spiritual magnet and role model not only for his disciples, colleagues and university students, but also for the whole local pedagogical community (2).

Today, years later we are aware that the professor burned himself out like a candle too soon, to give us knowledge, to make us understand many things that were too difficult for us at that time (3).

He honourably wore his destiny built on work and humanity, and the sweet burden of goodness that never exausted him. At all stages of his life he showed professionalism, initiative, principledness, goodwill and allowed us to sip from the wellspring of knowledge and the multitude of qualities he possessed in order to become good specialists and enrich our patrimony of chosen feelings and life experience.

For us, his students, Professor Pavel Pulbere will remain an example of hard work, honesty and courage, a true national hero of professional sacrifice, but first of all - an epitome of a person of good faith.

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