The Activity of Natural Radionuclides Th-232, Ra-226, K-40, and Na-22, and Anthropogenic Cs-137, in the Water, Sediment, and Common Carp Produced in Purified Wastewater from a Slaughterhouse

Miloš Pelić 1, Željko Mihaljev 1, Milica Živkov Baloš 1, Nenad Popov 1, Ana Gavrilović 2, Jurica Jug-Dujaković 3 and Dragana Ljubojević Pelić 1, *  

1 Scientific Veterinary Institute “Novi Sad”, 21000 Novi Sad, Serbia  
2 Faculty of Agriculture, University of Zagreb, 10000 Zagreb, Croatia  
3 Sustainable Aquaculture Systems Inc., 715 Pittstown Road, Frenchtown, NJ 08825, USA  
* Correspondence: dragana@niv.ns.ac.rs

Abstract: In the immediate vicinity of a slaughterhouse, a fishpond was built that uses treated wastewater from the slaughterhouse, and in this way integrates a new value chain in the form of purification and use of slaughterhouse wastewater in an aquaculture production system. The negative aspect of such integrated production systems is the concern related to the safety of fish meat produced in these systems. The aim of this research was to determine the activity level of Cs-137, K-40, Ra-226, Th-232, and Na-22 in water, sediment, and carp harvested from a pond that received purified water from a slaughterhouse. All samples were collected in spring and in autumn. The activity concentrations of selected radionuclides were determined by gamma spectrometry (HPGe detector). The activity of K-40 in water samples ranged from 8.4 to 15.6 Bq L⁻¹. The specific activity concentrations of the Ra-226 in water samples ranged between 1.02 ± 0.11 and 2.76 ± 0.49 Bq kg⁻¹. The results of the activity of natural radionuclides (Bq kg⁻¹) in the sediment samples were in the following ranges: 440–629 for K-40, 10.7–15 for Th-232, 20.2–44.4 for Ra-226, and 1.08–2.04 for Na-22, with average values of 531.75, 12.3, 32.97, and 1.75, for K-40, Th-232, Ra-226, and Na-22, respectively. The average content of Th-232 (12.3 Bq kg⁻¹) did not exceed the world UNSCEAR average value of 45, while the average content of Ra-226 (32.97 Bq kg⁻¹) slightly exceeded the UNSCEAR value of 32 Bq kg⁻¹. The K-40 concentration activity of 531.75 Bq kg⁻¹ was much higher than the UNSCEAR weighted average value of 420 Bq kg⁻¹. In the fish samples, natural radionuclide Na-22 was detected only in autumn (2.74 ± 0.32 Bq kg⁻¹). Results of Cs-137 and Th-232 concentrations were below the method detection limit in all samples, <0.5 Bq kg⁻¹ and <2 Bq kg⁻¹, respectively. The activity of K-40 was in the range from 121 to 160 Bq kg⁻¹. The activity concentrations of the Ra-226 in carp samples ranged between 9.5 and 54.4 Bq kg⁻¹. The results indicate that consumption of fish meat obtained from this integrated system does not pose a significant health concern in the case of the usual consumption rate that is typical for the population of Serbia. Almost no statistically significant seasonal variations were observed.

Keywords: integrated system; sustainable aquaculture; freshwater fish; radionuclides; monitoring

1. Introduction

The global slaughterhouse industry is a very important industrial sector that earns significant profit. However, it faces several problems, among which, the most important, globally, is environmental pollution due to large amounts of wastewater generated during all stages of production [1]. Purification of water from the slaughterhouse is very important from an ecological point of view, and there is no alternative to complying with legal regulations and preserving the environment. The use of wastewater from the slaughterhouse...
in another production process can contribute to the preservation of the environment and the sustainability of the slaughterhouse industry. The production of fish in treated slaughterhouse wastewater could be an ecological solution for the sustainable use of organically laden water used in slaughterhouses [2]. This is particularly important if we consider that a regular and adequate water supply is essential for the sustainability of aquaculture. Many types of integrated systems for fish farming and other forms of agricultural or industrial production have been known for centuries in different parts of the world [3–5]. Integrated production means connecting several independent production processes into a system based on the principle that a by-product or waste from one production process can be an input component for another. The possibilities of integrated production are very large. An integrated system of fish farming in combination with other types of industrial, agricultural, and livestock production is a unique and cost-effective system that ensures higher incomes, contributes to the availability of relatively cheap sources of protein and other nutrients, and increases productivity on relatively small ponds. Recycling waste from industrial plants or farms is an important component of an integrated fish production system, as it improves the economy of production, strengthens the local economy, and reduces the negative impact on the environment [6,7]. On the other hand, such a method of production always carries certain risks, especially when it comes to the safety of the produced fish, and it is necessary to examine all aspects of the use of wastewater from slaughterhouses for fish farming and possible further use of water from ponds for irrigation. In recent years, there has been increasing concern about radioactive contaminants in the environment from livestock production systems [8]. Agricultural or free-range-reared domestic animals may be contaminated with radionuclides from the environment through a variety of different channels. Furthermore, some radionuclides are environmentally mobile and could be transferred to animals. Some elements can be accumulated in animal tissue over time and, in many slaughterhouses, animals of different ages, particularly cattle, are slaughtered, which can significantly contribute to the concentration of radioactive elements in the wastewater from the slaughterhouse. Radioactive elements could be in wastewater as a consequence of contamination from contaminated animals during slaughtering. Consequently, wastewater may contain radioactive materials and pose a risk to the aquatic ecosystem [9]. When contaminants enter the water, they accumulate in the sediment, and then the sediment becomes a sink for contaminating the aquatic environment and fish. Slaughterhouses are potentially a minor but continuous source of natural radionuclides, bearing in mind that slaughtered animals come from different places and that through grazing and/or food they have accumulated a certain number of natural radionuclides that pass into the water during production and washing, and that such waste is discharged into environment. Nonetheless, slaughterhouses have been neglected in research. To understand the exposure of people to radionuclides from natural and anthropogenic sources, it is very important to have relevant data on the level of radiation and the distribution of radionuclides in the environment. There is no nuclear power plant within the territory of the Republic of Serbia, but it should be mentioned that there are 15 nuclear power plants in neighboring countries, so the danger of possible radioactive contamination certainly exists. The main naturally occurring radionuclides include isotopes of uranium, thorium, and K-40 [10]. Anthropogenic activities such as gas and mineral exploration increase natural radioactivity to levels that could be of concern [11]. Cs-137 is an artificial radionuclide that is produced by fission. It belongs to the group of radionuclides of particular importance in freshwater and marine food chains. Artificial radioactive isotopes are present in the soil, are involved in the circulation of substances in nature, and accumulate in the human body through water, air, and food. They accumulate in bones and other tissues and lead to long-term radiation of the entire organism. Contamination of fish in fishponds may constitute a particularly significant pathway for human intake of Cs-137 by humans. Water from ponds should also be considered as a source of contamination. Sediment in all types of water (sea, rivers, lakes, fishponds) may be a source of contamination of aquatic organisms. Furthermore, contaminated sediment materials used as fertilizers may increase the radioactivity levels of
Cs-137 is a beta-gamma emitter and its half-life is 30.2 years. There is no specific critical target organ in which Cs-137 is deposited, and it is deposited in all cells of the body, since it is a chemical analog of potassium. The biological half-life of Cs-137 in humans ranges from 10 to 110 days, depending on age and metabolism [12]. Cs-137 did not exist in nature before the start of nuclear tests and nuclear disasters, and its concentration in European countries increased after the Chernobyl nuclear disaster in 1986 [13]. The presence of natural radioactive elements is also increasing due to anthropogenic activities. The production and diverse, frequent application of phosphorus fertilizers is one of the most important anthropogenic sources of environmental pollution with primordial radionuclides (U-238, Ra-226, Th-232, and K-40) [14–16]. Uranium, radium, and radon are soluble in water, and thorium is almost completely insoluble. Soluble elements dissolve in water and penetrate the sediment and consequently pollute the entire aquatic ecosystem and the aquatic organisms that live in it.

The use of appropriately treated wastewater has great potential in aquaculture, but there is still a major public health concern regarding the safety of fish produced in such systems. To date, several studies have been published on the safety of fish produced in purified wastewater from slaughterhouses, and the results have shown good production results. It has also been shown that the fish produced are safe from a microbiological point of view and in terms of pesticides and antibiotics, and that the health of the fish is not endangered by this way of production. In addition, it is known that fish can be a good bioindicator of environmental pollution [17–22]. Environmental contamination with radionuclides is a significant problem in modern society. There is no doubt that knowledge about the activity of radionuclides and their distribution is significant for assessing the risk of radiation exposure for the population. There is no information regarding the activity of radionuclides, especially significant radionuclides such as Cs-137, in fish produced in purified wastewater from slaughterhouses, or in the water and sediment from such systems, although such systems represent sustainable solutions for the food industry, as well as for fish farming. The main aim of this research was to evaluate the activity of Cs-137, K-40, Ra-226, Th-232, and Na-22 in the water, sediment, and common carp produced in treated wastewater from a slaughterhouse. Additionally, all samples were analyzed over the course of two sampling periods in order to detect any potential seasonal variations in the activity of radionuclides.

2. Materials and Methods

An integrated system consisting of a slaughterhouse, a water treatment system, and an earthen pond (Figure 1) was installed in the village of Pećinci (N 44.860783, E 19.957004), Republic of Serbia. The fishpond was continuously filled with purified water from the slaughterhouse and additionally with well water, and aeration of the pond was ensured. After being discharged from the slaughterhouse, the water is purified in the purification system and transported to the pre-fishery pond where the aerators were installed. The water is then transported to the fishpond where the carp are raised, and then the water from the pond is transported to the irrigation canal and is used to irrigate the surrounding crops near the slaughterhouse. In this way, a fully closed circular production system is obtained. Details related to the design of the system, the breeding of carp in this system, and these system’s production results are presented in the paper published by Pećić et al. [17]. The fishpond is continuously aerated and fed with purified wastewater from a slaughterhouse, in addition to well water. The proportion of well water to treated water was roughly 2:1. A total of 2500 individuals/ha of two-year-old common carp that were acquired from a commercial fishpond were stocked in the first year. Carp began with an average weight of 200 g. The survival rate was 74% at the end of the first year. The first sampling was conducted in spring of the next year, and the second was conducted in autumn of the same year, or at the end of the experimental period. The survival rate in the second year was 87%. Seven samples of two-year-old carp were harvested from a pond with treated wastewater in spring and autumn at the end of the growing season. Fish were caught by dragging the net on the pond. Additionally, samples of both sediment and water were collected for
study during both seasons. Water samples were taken in 1000 mL plastic bottles. Water sampling was carried out at five points: water from the purifier, water from the outlet of the purifier, water from the pre-fishery pond, water from the fishpond, and water from the irrigation canal. Sediment was sampled in plastic containers with a volume of 5 L.

Figure 1. Scheme of the integrated system.

The presence of radionuclides in samples of sediment, water, and fish meat was determined by applying gamma spectroscopic analysis of radionuclide activity. Gamma-spectrometric analysis of carp meat was carried out without prior sample preparation. The sample for analysis was previously cleaned of any possible impurities and homogenized. The samples prepared in this way were placed in a special container for gamma spectrometric analysis—the so-called Marinelli sample containers of 250 mL, which are mostly made of plastic and are designed for the best measurement geometry, as well as the maximum efficiency of detector utilization. Gamma spectrometric measurements of the samples were taken using an accredited method, IARA TRS 295-1989 [23], and a coaxial HPG-e detector (Ortec, Oak Ridge, TN, USA), with relative efficiency of 28% and energy resolution of 1.67 keV at the energy 1.33 MeV of isotopes 60 Co. The detector is protected by a 10 cm thick cylindrical lead shield. The lead housing is internally coated with cadmium, copper, and plexiglass adsorbent. The recorded gamma spectra were analyzed using a multi-channel analyzer with an analogue–digital converter having memory of 16,384 channels using the software GammaVision 8.10 (ORTEC®, Oak Ridge, TN, USA). Isotope activity concentrations from all recorded gamma lines were calculated after background subtraction, and measurement uncertainties were presented at a 95% confidence interval. Water samples were prepared and packed in cylindrical Marinelli containers (V = 1000 mL). The typical measurement time was 100 ks. Energy and efficiency calibrations were conducted using standard reference material Source No. LR 320 certified by the Calibration laboratory for radioactivity measurement (Deutscher Kalibrierdienst, Braunschweig, Germany). The specific activity of $^{226}$Ra was determined from the gamma rays at 609.3, 1120.3, and 1764.5 keV of $^{214}$Bi and 295.2 and 351.9 keV of $^{214}$Pb. Specific activities of $^{40}$K and $^{137}$Cs were determined using their own 1460.8 keV and 661.7 keV gamma rays, respectively. The measured specific activity of $^{137}$Cs was decay-corrected to the sampling date. Gamma rays with energies 911.2 and 969.0 keV ($^{228}$Ac) and 238.6 keV ($^{212}$Pb) were used for the calculation of the specific activities of $^{232}$Th. Concentration activity of $^{22}$Na was determined using its gamma line at 511.0 keV. The output signal was processed by a multi-channel analyzer 92x-II Spectrum Master, and the obtained spectra were analyzed by Gamma Vision 32 software (version 5.3). The results of the interlaboratory comparison organized by the
IAEA are presented as an example of quality control in order to ensure the accuracy of the results (Table 1).

Table 1. Results of participation in IAEA interlaboratory exercises. Samples analyzed were water, fish flesh, and soil samples.

<table>
<thead>
<tr>
<th>Tested Radionuclide</th>
<th>Type of Sample</th>
<th>Target Value (IAEA) [Bq/kg]</th>
<th>Measured Value [Bq/kg]</th>
<th>Precision [%]</th>
<th>Accuracy [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>137Cs</td>
<td>Water (spiked)</td>
<td>64.4 ± 0.9</td>
<td>66.2 ± 2.9</td>
<td>3.95</td>
<td>102.8</td>
</tr>
<tr>
<td></td>
<td>Fish</td>
<td>18.9 ± 1</td>
<td>19.3 ± 1.4</td>
<td>4.08</td>
<td>102.1</td>
</tr>
<tr>
<td>22Na</td>
<td>Water (spiked)</td>
<td>76.8 ± 1.2</td>
<td>72.7 ± 3.6</td>
<td>3.34</td>
<td>94.7</td>
</tr>
<tr>
<td>40K</td>
<td>Fish</td>
<td>369 ± 18</td>
<td>376 ± 25</td>
<td>3.98</td>
<td>101.9</td>
</tr>
<tr>
<td></td>
<td>Soil</td>
<td>374 ± 15</td>
<td>406 ± 27</td>
<td>4.11</td>
<td>108.6</td>
</tr>
<tr>
<td>226Ra</td>
<td>Soil</td>
<td>31.2 ± 1.5</td>
<td>29.1 ± 2.3</td>
<td>4.80</td>
<td>93.3</td>
</tr>
<tr>
<td>232Th</td>
<td>Soil</td>
<td>33.6 ± 3.3</td>
<td>31.6 ± 1.6</td>
<td>4.66</td>
<td>94.0</td>
</tr>
</tbody>
</table>

The precision and accuracy of the method were tested using certified reference material LR 320 (Deutscher kalibrierdienst, Berlin, Germany).

To assess the risk to human health, the quality of fish for human consumption was analyzed. The content of radionuclides was compared with the certified guidelines for human food safety recommended for fish in Serbia [24]. We also estimated the dose of radionuclide intake according to the formula [25].

For adults, the recommended dose conversion coefficients gT,r for K-40, Cs-137, and Na-22 are $6.2 \times 10^{-9}$ Sv Bq$^{-1}$, $1.3 \times 10^{-8}$ Sv Bq$^{-1}$, and $3.2 \times 10^{-9}$ Sv Bq$^{-1}$, respectively [26].

The data were analyzed using the Excel (Microsoft Office 2013) software, v. 15.0 package with the Data Analysis plug-in. The data are shown as mean values ± SD. The results obtained for samples collected in spring and autumn were compared using Student’s t-test. Differences were considered significant at the $p < 0.05$ significance level.

3. Results and Discussion

The results of activity of Cs-137, K-40, Ra-226, Th-232, and Na-22 in the samples of water, sediment, and fish from the integrated system of fish production are shown in Tables 2–4. There are very little literature data on the presence of radionuclides in the pond ecosystem and fish. Mihaljev et al. [27] conducted a study of the concentration of radionuclides in samples collected from three locations of the Danube River, two ponds and one lake on Fruška Gora, in which six types of fish (catfish, perch, pike, carp, carp, and carp) were examined. In the research of Janković-Mandić et al. [28], the presence of Cs-137 was determined in all samples of uncultivable land from the area of the city of Belgrade. Large variations in the specific activity of the radionuclide, as well as the dose derived from it, were determined, which were attributed to spatial differences in the physical-chemical and biological properties of the soil, the soil type, and the fauna.

The activity of K-40 in water samples ranged from 8.4 to 15.6 Bq L$^{-1}$. No statistically significant seasonal variations were observed, with the exception of K-40 in water from the pre-fishery pond where a significantly higher level of activity was observed in autumn. In sediment, it ranged from 440 to 629 Bq kg$^{-1}$. There are some locations, such as areas in China, Austria, India, and Brazil, that have high levels of background radiation [29]. The activity concentration for K-40 in our study varied widely and was significantly lower compared to the measured concentration in India, where the highest K-40 activity reached 2531 Bq kg$^{-1}$ [29], which was higher than the mean concentration activity (324 Bq kg$^{-1}$) observed in cement samples in Turkey [30]. Shetty et al. [31] reported that activities for K-40 varied from 162.64 Bq kg$^{-1}$ to 2461 Bq kg$^{-1}$. Our results also further indicate that the radionuclide K-40 concentration is not uniformly distributed in both water and in sediment samples. The concentration values for K-40 are within the range of the activity measured in various regions of the world. No statistically significant seasonal variations were found.
for sediment samples, with the exception of Cs-137, which was significantly higher in sediment in the vicinity of the treatment plant, and sediment from fishpond 1 in autumn in comparison with sediment samples from spring. Furthermore, activity of K-40 was higher in spring than in autumn and the difference was statistically significant.

Table 2. Activity of radionuclides in water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water from Purifier</th>
<th>Water After Purifier</th>
<th>Water from Pre-Fishery Pond</th>
<th>Water from Fishpond 1</th>
<th>Water from Channel for Irrigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs-137 (Bq/L)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&lt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>K-40 (Bq/L)</td>
<td>10.0±2.0</td>
<td>8.4±0.5</td>
<td>11.3±1.5</td>
<td>15.6±1.2</td>
<td>10.6±1.1</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&lt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>Ra-226 (Bq/L)</td>
<td>1.92±0.30</td>
<td>1.16±0.22</td>
<td>1.02±0.11</td>
<td>2.76±0.49</td>
<td>2.50±0.61</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>Th-232 (Bq/L)</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>&lt;3</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>Na-22 (Bq/L)</td>
<td>0.87±0.11</td>
<td>0.60±0.10</td>
<td>1.12±0.31</td>
<td>1.34±0.40</td>
<td>0.95±0.36</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
</tbody>
</table>

All values are presented as mean ± standard deviation (n = 3); p<0.05 (bold)—statistically significant difference; p>0.05 (no bold)—statistically insignificant difference.

Table 3. Activity of radionuclides in sediment samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sediment in Vicinity of Treatment Plant</th>
<th>Sediment from Pre-Fishery Pond</th>
<th>Sediment from Fishpond 1</th>
<th>Sediment from Fishpond 2</th>
<th>Sediment from Channel for Irrigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs-137 (Bq/kg)</td>
<td>&lt;0.5</td>
<td>2.84±0.17</td>
<td>4.81±0.14</td>
<td>7.66±0.23</td>
<td>4.76±0.13</td>
</tr>
<tr>
<td></td>
<td>p&lt;0.05</td>
<td>p&gt;0.05</td>
<td>p&lt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>K-40 (Bq/kg)</td>
<td>457±55</td>
<td>544±10.0</td>
<td>514±9.0</td>
<td>629±11.0</td>
<td>440±8.0</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&lt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>Ra-226 (Bq7 kg)</td>
<td>31.2±4.8</td>
<td>25.0±0.7</td>
<td>44.4±5.2</td>
<td>42.3±5.1</td>
<td>20.2±1.1</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>Th-232 (Bq/kg)</td>
<td>11.3±0.4</td>
<td>10.7±0.4</td>
<td>12.6±0.71</td>
<td>15.0±2.9</td>
<td>10.9±0.22</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td>Na-22 (Bq/kg)</td>
<td>2.06±0.14</td>
<td>1.99±0.14</td>
<td>2.04±0.18</td>
<td>1.92±0.20</td>
<td>1.08±0.30</td>
</tr>
<tr>
<td></td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
<td>p&gt;0.05</td>
</tr>
</tbody>
</table>

All values are presented as mean ± standard deviation (n = 3); p<0.05 (bold)—statistically significant difference; p>0.05 (no bold)—statistically insignificant difference.
Table 4. Activity of radionuclides in carp samples (n = 7) in spring and autumn.

<table>
<thead>
<tr>
<th>Radionuclides</th>
<th>Spring</th>
<th>Autumn</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs-137 (Bq/kg)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>/</td>
</tr>
<tr>
<td>K-40 (Bq/kg)</td>
<td>144.75 ± 16.32</td>
<td>138 ± 17.11</td>
<td>p &gt; 0.05</td>
</tr>
<tr>
<td>Ra-226 (Bq/kg)</td>
<td>25.72 ± 18.60</td>
<td>22.75 ± 8.15</td>
<td>p &gt; 0.05</td>
</tr>
<tr>
<td>Th-232 (Bq/kg)</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>/</td>
</tr>
<tr>
<td>Na-22 (Bq7 kg)</td>
<td>&lt;2</td>
<td>2.74 ± 0.32</td>
<td>p &lt; 0.05</td>
</tr>
</tbody>
</table>

All values are presented as mean ± standard deviation. p < 0.05 (bold)—Statistically significant difference; p > 0.05 (no bold)—statistically unsignificant difference.

The specific activity concentrations of Ra-226 in water samples ranged between 1.02 ± 0.11 and 2.76 ± 0.49 Bq kg⁻¹. In wastewater samples from power plants obtained by Janković et al. [32], the concentration of natural radionuclide Ra-226 was below the minimum detection activity (MDA). In comparison, the detected concentration of Ra-226 in drinking water in Pakistan varied within the range of 0.05–2.17 Bq L⁻¹, with an average of 1.09 Bq L⁻¹ [33], but the results obtained in Serbia were below 0.07 Bq L⁻¹ [34]. The activity concentration of Ra-226 in wastewater in Greece was 0.021–0.062 Bq L⁻¹ [35]. The Na-22 activities in our study ranged between 0.54 and 1.74 Bq L⁻¹ in water samples. In Serbia, there are no regulations about the allowed concentrations of radionuclides in waste and river water samples. According to current regulations [24], radioactivity concentrations in drinking water for Ra-226 should be below 0.49 Bq L⁻¹, and below 1 Bq L⁻¹ according to WHO [36]. According to our results, radionuclides are not effectively removed after treatment in a wastewater purification plant and this is consistent with previous results published by Ahmed et al. [37].

The activity of Cs-137 in the sediment samples ranged from 2.84 to 7.66 Bq kg⁻¹. A relatively large difference between the minimum and maximum measured values in the samples is characteristic of pollutants of anthropogenic origin. The results of the research by Krstić et al. [38] showed that Cs-137 binds to the surface layer of the soil, up to a depth of 10 cm, and that its concentrations decrease with depth. According to results obtained by Janković-Mandić et al. [28], the specific activity of Cs-137 in the soil samples collected from different locations in Belgrade was in the range of 3 to 87 Bq kg⁻¹, with the mean value of 23 Bq kg⁻¹. The authors explained that the expressed variability in activity of Cs-137 was a result of topographical differences and inhomogeneous surface contamination of the soil after the Chernobyl accident.

The results for natural radionuclides activity (Bq kg⁻¹) in the sediment samples are given in the following ranges: K-40 (440–629); Th-232 (10.7–15); Ra-226 (20.2–44.4); and Na-22 (1.08–2.04), with average values of 531.75, 12.3, 32.97, and 1.75, for K-40, Th-232, Ra-226, and Na-22, respectively. The average content of Th-232 (12.3 Bq kg⁻¹) does not exceed the world average value of 45 for Th-232 [39], while the average content of Ra-226 (32.97 Bq kg⁻¹) slightly exceeds the UNSCEAR value of 32 Bq kg⁻¹. The K-40 concentration activity of 531.74 Bq kg⁻¹ is much higher than the UNSCEAR weighted average value for K-40 of 420 Bq kg⁻¹. Similar results were obtained by Radomirović et al. [40]: 35 Bq kg⁻¹ for Th-232 and 580 Bq kg⁻¹ for K-40, by analyzing surface sediment from the Boka Kotorska Bay (Adriatic Sea).

The assessment of the activity of radionuclides in the fish samples in spring and autumn from our integrated system of production are shown in Table 4. Natural radionuclide Na-22 was detected only in autumn (2.74 ± 0.32 Bq kg⁻¹). Results of Cs-137 and Th-232 concentrations were below the method detection limit in all samples, i.e., <0.5 Bq kg⁻¹ and <2 Bq kg⁻¹, respectively. The activity of K-40 in the present study was in the range from 121 to 160 Bq/kg. In the research conducted by Mihaljev et al. [27] and Milenković et al. [41], it was in the interval from 118 to 190.44–165 Bq kg⁻¹, respectively. The activity concentration of K-40 obtained by Vitorović et al. [42], was lower compared to results obtained by Mihaljev et al. [27]: 85 ± 3 (white fish), 93 ± 3 (catfish), 94 ± 4 (carp fish), and 98 ± 7 (pike perch) Bq kg⁻¹.
The activity concentrations of Ra-226 in carp samples ranged between 9.5 and 54.4 Bq kg\(^{-1}\), which is in agreement with Ademola and Ehiedu [43], who observed similar results analyzing freshwater fish, i.e., from 21.4 ± 3.8 Bq kg\(^{-1}\) (\textit{Clarias anguillaries}) to 38.6 ± 11.6 Bq kg\(^{-1}\) (\textit{Gymnarchus niloticus}) [43]. Our numbers are much higher than those in the results given by Antović and Antović [44].

By analyzing the available literature and data on Cs-137 activity levels in different countries, it could be seen that higher activity was measured in countries that were exposed to the radioactive cloud from Chernobyl, such as Serbia [28,42,45], Republic Srpska [46], Croatia [47], Republic of Macedonia [48], and Turkey [49]. The activity of Cs-137 in Serbia ranged from 3 to 87 [28], in the Republic of Macedonia from 2 to 358 [48], and in Croatia from 36 to 326 [47]. In Turkey, it varied from 1 to 153 [49–51], and in the Republic Srpska it ranged from 2 to 68 [46]. In other parts of the world lower values of Cs-137 activity are measured and in these countries its activity is mainly associated with above-ground nuclear explosion and probes. In Saudi Arabia, the activity of Cs-137 was in the range from 0 to 3 Bq kg\(^{-1}\) [52], in Pakistan, it was 4 Bq kg\(^{-1}\) [53], in Egypt it ranged from 2 to 9 [54], in India it ranged from <0.1 to 10 Bq kg\(^{-1}\) [55,56], and in China it ranged from 1 to 6.4 [57]. According to a report published by the Secretariat of Environmental Protection, Belgrade, City Institute of Public Health, Belgrade, and the Regional Environmental Center for Central and Eastern Europe (REC) for the year 2011 [58], the majority of the radioactivity in river water originated from natural radionuclides (mainly K-40), and the activity of long-lived radionuclides of artificial origin (Cs-137 and Sr-90) was at significantly lower levels. The activity of Cs-137 in sediment was in the range from 7.7 to 42.2 Bq kg\(^{-1}\) dry matter. It is estimated that this activity is linked to the contamination caused by the nuclear accident in Chernobyl in 1986. The activity of Sr-90 was in the range from 0.08 to 0.39 Bq kg\(^{-1}\) of dry matter. This activity is also attributed to the contamination caused by the nuclear accident in Chernobyl in 1986. According to the above-mentioned report, the specific activity of Cs-137 (Bq kg\(^{-1}\)) in the river sediments from rivers in Belgrade was as follows: the minimal annual value in the sediment from the river Sava was 7.7 ± 0.8 and in the sediment from the Danube River was 7.8 ± 0.8. The average annual value of activity in sediment from the river Sava was 21.5 ± 15.7, and in the sediment from the Danube River 13.5 ± 7.2. The maximum annual value of the activity measured in the sediment of the river Sava was 42.2 ± 1.3, and that in the sediment from the river Danube was 24.1 ± 0.7 Bq/kg. In the Report of the Secretariat of Environmental Protection, Belgrade, City Institute of Public Health, Belgrade, and the Regional Environmental Center for Central and Eastern Europe (REC) for the year 2011 [58], the values of the radioactivity in the samples of non-arable land in Belgrade are also included. Due to the long half-life of Cs-137, its activity in the soil samples was still significant. The measured activity of Cs-137 in non-arable land ranged from 0.9 Bq kg\(^{-1}\) to 26.1 Bq kg\(^{-1}\), while in the arable land, it ranged from 5.9 Bq kg\(^{-1}\) to 65.4 Bq kg\(^{-1}\). The results for Cs-137 (Table 2) show the highest value is for sediment from the fishpond (7.66 ± 0.23 Bq kg\(^{-1}\)). These Cs-137 values are much lower than 600 Bq kg\(^{-1}\), which is the EU upper limit for Cs-137 allowed in food [59]. Therefore, it is unlikely that fish growing in ponds on these soils could accumulate dangerously high concentrations of Cs-137.

The dose coefficients for adults are 6.2 × 10\(^{-9}\) Sv Bq\(^{-1}\) for K-40 and 2.8 × 10\(^{-7}\) Sv Bq\(^{-1}\) for Ra-226 [26]. The total committed effective doses for adults and children are far lower than the world average values of 0.29 mSv y\(^{-1}\) [39], and lower than the recommended total annual effective dose of 1.0 mSv y\(^{-1}\) set by ICRP [60] as the maximum acceptable level for the members of the public.

Regulation on the limits of radionuclide content in drinking water, food, feed, medicine, objects of general use, building materials, and other goods placed on the market [24] set up the prescribed limits of radionuclide content in drinking water, foodstuffs, animal feed, drugs, general purpose goods, building materials, and other goods placed on the market. Regulations on the monitoring of radioactivity [61] include the manner and conditions of systematic examination of radioactivity in the environment and in the environment around
nuclear facilities. According to the regulations on limits of radionuclide content in drinking water, food, feed, medicine, objects of general use, building materials, and other goods placed on the market [24], the limit of the content of Cs-137 in fish is 150 Bq kg$^{-1}$. Based on these results, carp produced in ponds supplied with treated wastewater from slaughterhouse industries is safe for human consumption from the point of view of Cs-137 activity.

There are no existing standards that could be applied to the radiological quality of water in the fishpond. Therefore, when the obtained values of the concentration of the radionuclide activity of Cs-137 in the water samples from the ponds are compared with the concentration of radionuclides of 1000 mBq L$^{-1}$ for Cs-137, which is valid for drinking water, it can be concluded that the investigated water is free of radiation, and that the content of the radionuclides therein is below the maximum allowable values.

Integrated system radioecology is a very complex field of research due to several relevant factors and further research is needed to reach some conclusions. The obtained results can serve as a basis for further research and for monitoring the level of radioactivity in integrated production systems.

4. Conclusions

By comparing the obtained values for the activity of Cs-137 with the results of previous studies conducted within the territory of the Republic of Serbia, and in different countries worldwide, it can be concluded that all the measured values of the activity of Cs-137 are within the acceptable limits for the territory of Serbia, and also within the acceptable limits recommended by various globally relevant organizations, including WHO. Analysis of the activity of Cs-137 radionuclides in the sediment showed that the values are within the allowable limits of normal, natural values. It can therefore be concluded that the sediment from the pond is not radiologically loaded.

Based on the obtained results, carp produced in a pond supplied with optimally purified wastewater from slaughterhouse industries is safe for human consumption from the point of view of radionuclide activity. It can be concluded that the investigated water is free of radiation and that the sediment from the pond is not radiologically loaded. The results indicate that consumption of fish meat obtained from this integrated system does not pose a significant health concern in the case of the usual consumption rate that is typical for the population of Serbia.

Continuous monitoring of the activity of radionuclides in aquatic environments and fish species reared in purified wastewater is very important, bearing in mind that fish is both an important food source and an important indicator of environmental contamination.

Author Contributions: Conceptualization, M.P. and M.Ž.B.; methodology, Ž.M.; validation, Ž.M., formal analysis, N.P.; investigation, M.P.; data curation, M.Ž.B.; writing—original draft preparation, D.L.P.; writing—review and editing, A.G. and J.J.-D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science, Technological Development and Innovation of Republic of Serbia by the Contract of implementation and funding of research work of NIV-NS in 2023, Contract No: 451-03-47/2023-01/200031.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest. The study’s design, data collection, analysis, and interpretation, the drafting of the report, and the decision to publish the findings were all done independently from the funder.
References


7. Xu, Q.; Dai, L.; Gao, P.; Dou, Z. The environmental, nutritional, and economic benefits of rice-aquaculture animal coculture in China. Energy 2022, 249, 123723. [CrossRef]


26. ICRP. Compendium of dose coefficients based on ICRP publication 60. In ICRP Publication 119. Annual ICRP 41 (Suppl. 1); ICRP: Ottawa, ON, Canada, 2012.


29. Derin, M.T.; Vijayagopal, P.; Venkatraman, B.; Chaubey, R.C.; Gopinathan, A. Radionuclides and radiation indices of high background radiation area in Chavara-Neendakara placer deposits (Kerala, India). *PLOS ONE* 2012, 7, e50468. [CrossRef]


41. Milenković, B.; Stajic, J.M.; Stojic, N.; Pucarević, M.; Strbac, S. Evaluation of heavy metals and radionuclides in fish and seafood products. *Chemosphere* 2019, 229, 324–331. [CrossRef]


45. Sarap, N.B.; Janković, M.M.; Todorović, D.J.; Nikolić, J.D.; Kovačević, M.S. Environmental radioactivity in southern Serbia at locations where depleted ura-nium was used. *Arh. Hig. Rada Toksikol.* 2014, 65, 189–197. [CrossRef]


**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.