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Editorial

Finally, after much effort, the second edition of the journal has been issued. In the meantime, however, several things have happened.

First you can see that the name of the journal has been changed. Several names were considered regarding the journal's scope and the expectations of the editorial board. The name has to reflect the policy of the journal on the one side and goals on the other. Therefore the name **Sanitarno Inženirstvo International Journal of Sanitary Engineering Research** was finally chosen.

International means that all issues will be in the English language and available to experts, researches and readers worldwide who are working on or are professionally and voluntarily interested in topics like occupational health and safety, environmental engineering, environmental phenomena and environmental protection.

Sanitary Engineering is a common name in the area of former Yugoslavia for Occupational Health and Safety which includes additional topics like food safety, influence of chemicals and waste on food quality and health, on conserving the environment, on impact of human activities on the environment etc. This means that sanitary engineers are experts who have the basic knowledge of engineering and medical sciences. It should be pointed out that the journal is also the official paper of the Chamber of Sanitary Technicians and Engineers of the Republic of Slovenia.

Research means that papers published in this journal reflect research endeavors on the above mentioned topics not only in Slovenia but also in other countries.

Another point that should be made is that this journal has the potential to link professionals, experts and researches from all former Yugoslav republics: from Bosnia and Herzegovina, Croatia, Macedonia, Monte Negro and Slovenia. During this short period of the journal's existence several connections and cooperations have been established between researches from these Balkan countries. The present issue contains scientific and professional papers from Slovenian authors only. But the next, namely the third issue should contain papers of authors from Croatia and hopefully also from other Balkan countries.

The current issue contains the research results mainly from two fields: environmental protection and food safety. The papers deal with the impact of waste dumps on the groundwater of Ljubljansko polje, they present the research results of the metals removal from wastewater through different substrates in the wetlands, the current practices of food handlers in institutions and companies. An interesting topic is presented in the paper dealing with food tasting describing the procedures of doing it and with the recommendations for a testing procedure and methodology which should be standardised. The last paper contains the newest information on active hydrogen concentrations in juices and teas on the Slovenian market.

Janez Petek
Editor - in - Chief

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Content

Original scientific paper

Impact of illegal dumping sites on the groundwater of Ljubljansko polje

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ABSTRACT:

Due to dense settling and the concentration of numerous economic and other activities, gravel aquifers are threatened. The key conflict on Ljubljansko polje is between the need to protect the groundwater as a source of drinking water for the supply of Ljubljana on one hand and agriculture and various urban-related activities on the other. We used a survey to register and study 1,445 illegal dumping sites in the narrowest and narrow water protection areas, of which Jarški prod on the left bank of the Sava River near Črnuče, the most problematic area, alone has 151 ones. The total surface area of the studied illegal dumping sites amounts to 120,816 m^2, and their total volume is 209,422 m^3. In the area surveyed, we also registered 100 gravel pits, 58 information signs, and 57 road barriers. Two thirds of the waste consists of construction material. A good seventh of the waste is hazardous waste. On Jarški prod, the total surface area of the waste is 26,273 m^2, which means that waste covers 1.2 % of the area. This makes Jarški prod one of the most waste-contaminated areas in Slovenia. An average dumping site on Ljubljansko polje measures 178 m^2, and the total volume of waste amounts to 42,464 m^3. Using a carefully developed methodology, we have planned a priority schedule for the remediation of illegal dumping sites.

KEY WORDS:

Illegal dumping sites, Groundwater, Water protection area, Remediation, Ljubljansko polje, Jarški prod

INTRODUCTION

Gravel plains and the development of cities have long shared a common history in Central Europe since the majority of cities developed beside the major rivers and their tributaries that created these plains [1]. The forces of nature that had previously shaped these areas acquired a rival, man, who more or less intensively intervened in the natural course of events. He reshaped them according to his needs and according, of course, to the level of technical and technological development.

The results of natural and social processes depend on their duration and intensity. Over a longer period, the impacts of minor changes can become blurred, which means a return to the original state. In the event of more radical and lasting changes, the old landscape systems have acquired new contents [2]. Among man's encroachments, urbanization has a special role, since it causes substantial changes in the environment and its structure.

Modern cities in economically developed countries deviate substantially from the concepts of sustainable development because their activities and populations need extensive land to meet their material and energy demands and for dumping various emissions and wastes.

On one hand, in the irregular relief of Slovenia, gravel plains with aquifers of intergranular porosity are the most important source of drinking water, supplying water to more than 90 % of the population, and on the other, they comprise the economic, traffic and settling core of the country [3]. Modern cities in economically developed countries (and Ljubljana is no exception here) deviate substantially from the concepts of sustainable development because their activities and populations need extensive land to meet their material and energy demands and for dumping various emissions and wastes. Here, they inevitably confront the limitations of ecosystems. The capability of an ecosystem is limited by a three-dimensionally conceived space that includes supplies of natural resources (non-renewable, conditionally renewable, and renewable) and the capacity to absorb waste, pollution, and encroachments on the environment [4]. The degradation of the urban landscape is therefore the consequence of incomplete cycles of matter (e.g. waste) [5,6].

Over the last few decades, Ljubljana has expanded onto former farming land. Crowded roads run in the immediate vicinity of pumping stations, and the area directly along the Sava River has no particular activity aside from the pumping stations, which encourages the illegal waste dumping. The area is easily accessible and crisscrossed by dirt roads, and unpermitted activities are further encouraged by unclear ownership of the land. Numerous abandoned and unrehabilitated gravel pits attract dumping. The main cause of this environment-unfriendly situation is undoubtedly the lack of a mature relationship with the living environment [7].

A cadastre of dumping sites previously existed. In September 1996, the Oikos company surveyed the entire area of the City Municipality of Ljubljana and registered 457 dumping sites with a total volume of 32,782 m^3 [8]. The Bion company also performed a study at the level of the entire municipality, in which the data was processed according to district communities. They studied 278 illegal dumping sites with an estimated total volume of 100,000 m^3 [9]. In all those studies, the limit value for a registered dumping site was one cubic meter of waste. An interesting fact is that according to the cited data the number of dumping sites supposedly decreased by almost 40 % between 1996 and 2004 while the quantity of waste supposedly increased by more than three times, which is probably the result of differing levels of thoroughness in carrying out the surveys.

At the request of the inspection authorities the Snaga company in the last six years (2000-2005) has removed a total of 36,499 m^3 of communal waste from all the illegal dumping sites in the City Municipality of Ljubljana.

Despite the uniform criteria of registering dumping sites with at least one cubic meter of waste, a comparison of various surveys of the area of the entire City Municipality of Ljubljana or its individual parts appears to establish considerable discrepancies. Table 1 presents a comparison of the results of surveys made in 1996 (Oikos d.o.o.) [8], 2000 (Kušar 2000) [10], 2004 (Institute for Bioelectromagnetics and New Biology) [9], and 2006 (Anton Melik Geographical Institute Scientific Research Centre of the Slovenian Academy of Sciences and Arts (AMGI SRC SASA) [11].

Table 1.

Comparison of the results of various surveys of illegal dumping sites in the City Municipality of Ljubljana.

Year of survey	Area included	Surface area (km^2)	Number of surveyed illegal dumping sites	Estimated surface area (m^2)	Estimated volume (m^3)
1996	City Municipality of Ljubljana	275.0	457	70,448	32,761
2000	Open world of Ljubljansko polje	unknown	359	163,400	84,000
2004	City Municipality of Ljubljana	275.0	278	unknown	100,000
2006	Part of water protection area in the City Municipality of Ljubljana	45.8	1,482	122,573	211,279

The substantial differences obtained are probably the result of a number of factors: differences in the exactness of data collected, the subjectivity of surveyors, the variation of quantity and the season the data was collected (visibility is substantially better in winter without a snow blanket).

The fact that illegal dumping sites, especially in the vicinity of cities and water catchment areas, are very disturbing, even dangerous, raises the question of the need for their remediation. Since funding for complete remediation is usually not available, it is necessary to make a priority list of dumping sites to be rehabilitated on the basis of an assessment of their negative impact. This is where the question appears of whether it is possible to use a universal assessment methodology for all cases.

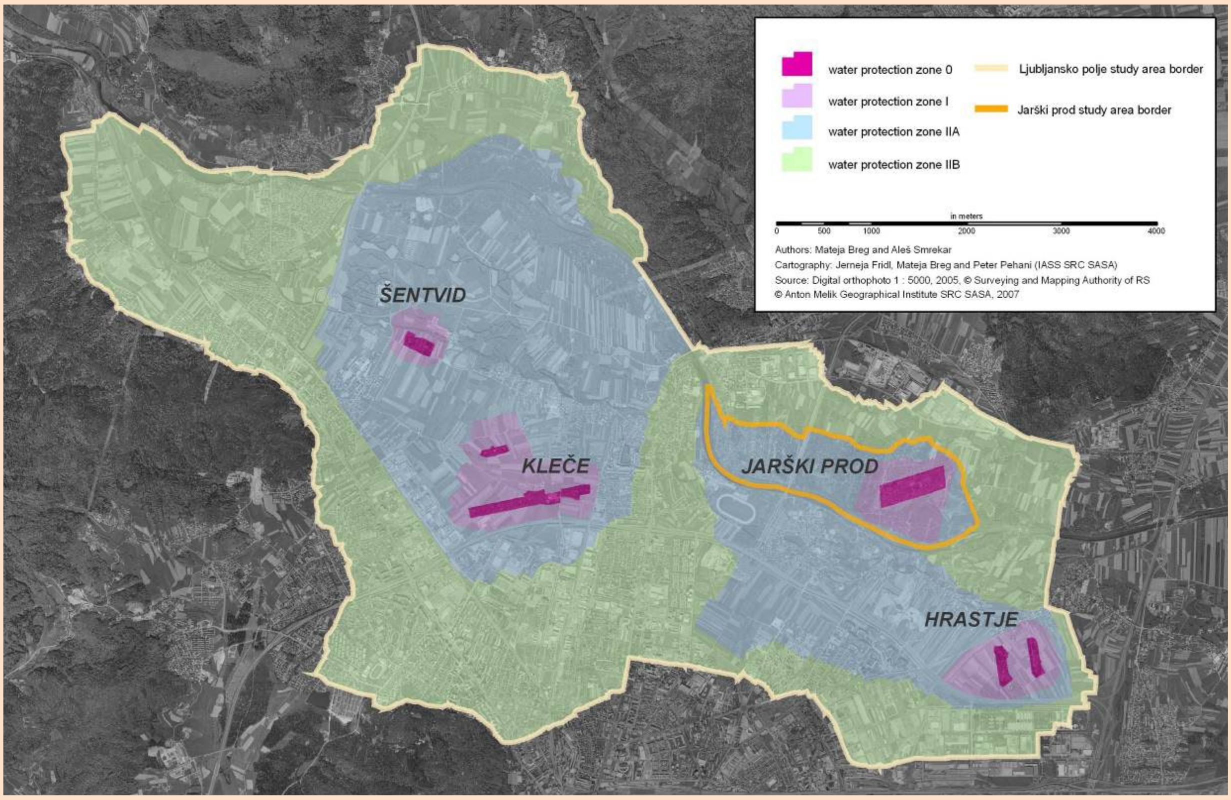
It is believed that this is possible to a certain extent and that the actual implementation depends primarily on the vulnerability and contamination of the specific environment, its land use, and last but not least on the quality of collected data that allows wide selection of applicable criteria. This paper presents one of the possibilities which have been used in the evaluation of illegal dumping sites in a smaller area where a very detailed description of dumping sites were made.

The area that in the past allowed environmentally-friendly activities could very soon become an environmental burden [12]. Although for the time being water analyses still indicate its suitability as a water source, the area of illegal dumping sites presents a hidden threat due to a past illegal dumping, which is still occurring to a smaller extent, since we have no knowledge of what is hidden under the surface. For a comprehensive and long-term successful solution of the problem, the remediation of the illegal dumping sites alone will not suffice; it will be necessary to re-establish the cultural and social values of the area and incorporate them into the permanent value system of the local population.

SURVEY OF THE STUDIED AREA

The City Municipality of Ljubljana supplies its population and companies from a number of water sources. Water started to flow in the first 606 of Ljubljana's houses on May 17, 1890, and the Kleče pumping station remains the heart of Ljubljana's pumping station system. In 1953, the Hrastje pumping station was opened, in 1955, the Šentvid pumping station, and in 1982, the Jarški prod pumping station [13]. The most extensive pumping sites of drinking water for the supply of Ljubljana are therefore situated on Ljubljansko polje, and its pumping stations are incorporated in the central pumping system. According to the Decree on the Water Protection Zone for the Aquifer of Ljubljansko polje [14], an area of 42.98 km^2 lies within the narrowest (0, I) and narrow (IIA, IIB) water protection areas (Figure 1).

Figure 1.
The narrowest and narrow water protection areas of drinking-pumping stations on Ljubljansko polje.



The cleansing capability of gravel and sand cover layers is effective with biological contamination but less so with chemical contamination because the sand for example does not restrain dung-water although it does neutralize acid. In general, the concentration of contaminatants decreases with the distance they travel through the ground. Soluble wastes, including fertilizers and certain industrial waste materials, cannot be removed by filtration, and metallic solutions are not susceptible to biological processes.

The quantity of groundwater contained in the aquiferous gravel-sand and conglomerate layers that fill the Ljubljansko polje basin is estimated at up to 100 million m^3. This is one of the largest reservoirs of undergorund water in Slovenia, a natural resource of regional importance. The depth of the groundwater depends on its water table and the height of the terrain. On a high terrace near Vižmarje the groundwater is found at a depth of more than thirty meters, while between Ježica and Zadobrova, at a depth of only five to ten meters. The annual regime of water table changes in the 1987–2005 period indicates considerable annual oscillation. In the Brod area, the oscillation spans 4 to 6 meters, around the Kleče pumping station 5 to 6 meters, and around the Hrastje pumping station 1.5 to 2 meters [15].

The four large legal gravel pits are located in Stanežiče, in the Dovjež area, southwest of the expressway intersection in Tomačevo, and in Obrije. They are all in the remediation phase.

The groundwater flows from the northwest to the southeast or east. In the western part of the aquifer, its velocity is between 5 m/day and 10 m/day, and in the eastern part, mostly between 10 m/day and 20 m/day [16].

The main source for the charging of the Ljubljansko polje aquifer is the Sava river, and the secondary source is the infiltration of precipitation water, which in places is considerably reduced due to urban land use [17]. In its upper part, the Sava charges the aquifer while in its lower part, the groundwater flows back into the river. The second largest surface watercourse on Ljubljansko polje is the Ljubljanica river. However, its flow is slow and its muddy bottom greatly limits the exchange of water between the river and the aquifer [16].

The vulnerability of the underground water depends on the hydrogeological, hydrological, and pedological conditions. Various construction works and excavations such as the excavation of gravel also have an impact on it. There are illegal gravel pits outside the consolidated urban area, especially on the lower terraces along the Sava River. The four large legal gravel pits are located in Stanežiče, in the Dovjež area, southwest of the expressway intersection in Tomačevo, and in Obrije. They are all in the remediation phase. Fortunately, the abandoned gravel pits were not filled up with large quantities of waste because after 1924, when organized waste collection started, the waste was transported mainly to the southern areas of Ljubljana [18].

From the analysis of changing land use [19] was concluded that urbanization is the most important cause of groundwater pollution. Urbanization has caused the amount of farm land to shrink distinctly, even though agricultural land use has spread ever closer to the Sava River [20]. Allotment gardeners, as a group with a large number of users of agricultural land, are having an increasing impact with their unique cultivation and other activities [21].

METHODS

We collected the majority of the data through field work, in which we recorded the most important anthropogenic elements linked to the degradation of the water protection area and the groundwater. We performed the field survey of the land during the winter when the visibility is substantially better since the vegetation is dormant. We focused on an inventory of surface objects [11, 22].

We itemized each individual heap of waste material with a volume of 1 m^3 or more as a separate dumping site. The inventory included both active and abandoned gravel pits. To draw attention to the inadequacy of legislative measures and the deep entrenchment of illegal dumping, we also registered warning and information signs and the barriers across access roads.

The surveyors entered the data on the properties and features of the dumping sites (e.g., visibility of the dump site, type of access, type of waste, estimation of the quantity of waste etc.) in specially prepared survey sheets on PDA's

We determined the position of individual objects on the terrain using a GPS (Global Positioning System) device and by taking a reading the Gauss-Krüger coordinates of centroids of illegal dumping sites and circumferences of gravel pits. The surveyors entered the data on the properties and features of the dumping sites (e.g., visibility of the dump site, type of access, type of waste, estimation of the quantity of waste etc.) in specially prepared survey sheets on PDA's (personal digital assistants). When the field work was complete, we merged the GPS measurements of locations and the attribute values from the survey sheets in a digital database that served as a basis for the further analyses. We further augmented the database with data acquired from the existing layers of data from various sources (e.g., water-protection areas, numbers of cadastral municipalities and parcels, names and surnames of owners of parcels).

Chemical sampling and analysis of waste

The general methodology used for planning a procedure for assessing the impacts on the environment due to illegal dumping sites is described in the US EPA document RCRA Facility Investigation (RFI) Guidance I-IV, 530/SW-89-031 [23]. The very extensive methodology was elaborated for the study of the most diverse types of contaminated sites and their impact on the environment, particularly on the groundwater. In a specific case, we methodologically used the part related to the impacts of illegal dumping sites. The methodology is somewhat outdated and probably less suitable for the needs of Slovenia. We also considered some modern European approaches to the assessment and remediation of contaminated sites for the protection of the environment from the impacts of hazardous substances elaborated in some international projects. These include:

CARACAS (Concerted Action on Risk Assessment for Contaminated Sites in the European Union, 1996–1998) [24]. The purpose of this project was to survey the current research in the field of degraded areas and to establish scientific priorities for further research on the improvement of the methodology of risk analysis of contaminated sites in Europe.

CLARINET (Contaminated Land Remediation Network for Environmental Technologies, 1999–2002) [25]. The following themes were examined: the regeneration of abandoned degraded areas, the impact of contaminated areas on water resources, technologies and techniques of remediation, aspects of impacts on human health, risk management, and support for decision-making.

RESCUE (Regeneration of European Sites in Cities and Urban Environments, 2002–2005) [26]. The main aim of the project was to develop and test a comprehensive approach to the sustainable regeneration of Europe's abandoned and degraded industrial areas. The suggested methodology is based on the sequence of the following two steps: a) the development of an analytical framework for determining sustainable goals and indicators, and b) the development of tools and recommendations for planning or taking measures in various circumstances.

We assessed the potential hazard of disposed waste on the basis of:

- physical-chemical properties of waste deposed (composition, solubility, stability, granulation);
- placement of deposal: surface – in contact only with meteorological water, surface – in contact with surface waters (lagoons, ponds), depth – in contact with groundwater;
- age of waste.

For sampling, we used the currently standard methods for sampling and preparation of a representative sample of soils on larger areas (ISO/TC 190/SC2, 2002). The methodology involves the division of the surface of the illegal dumping sites with a grid of suitable density (10–100) depending on the size of the area. The manual or machine excavation of material is then undertaken on a suitable number of selected microlocations determined by observations of the terrain and the material and any prior or existing information about possible dumping site sites (especially hazardous waste sites). The excavations cover the entire potential depth to the natural gravel base and even a little deeper. In the process, samples of the material are taken uniformly and notes are made on their observable characteristics (appearance, color, smell, consistency, and individual recognizable elements). The manual sampling was carried out to a depth of half a meter, which sufficed in most cases because the layers of waste were thin. Larger deposits were sampled with the use of a backhoe.

The manual or machine excavation of material is then undertaken on a suitable number of selected microlocations determined by observations of the terrain and the material and any prior or existing information about possible dumping site sites

The samples acquired from all of the sampling points at individual illegal dumping sites were combined, dried in the air at 40 °C, and sieved through a standard 2 mm sieve. We homogenized the fine fragments into a representative sample for analysis, while the rough fragments were weighed and discarded. We defined the prescribed parameters for the characterization of waste using the prescribed analytical methods for wastes and their standard leachates (SIST EN 12457:4).

For the assessment of the obtained results of waste analyses, we used the relevant limit values from the valid Slovene legislation on waste [27], which fully conforms with the environmental legislation of the European Union. We also complied with the limit values from the Rules on Soil Pollution Caused by Waste Deposits [28], which among other things refers to the environmental use of construction waste and excavations.

Establishing priority remediations

Establishing priority remediations of illegal dumping sites is done on the basis of carefully selected indicators that we judge to be of key importance from the viewpoint of the environmental issue of illegal dumping sites. The used remediation methodology was developed specially for this research. We combined nine selected indicators into four categories according to their assumed significance from the viewpoint of establishing priority remediation and determined appropriate weights for each.

We assigned different values or percentages to the individual categories and their indicators according to their significance in the total assessment of the necessity of the remediation of dumping sites (Figure 2).

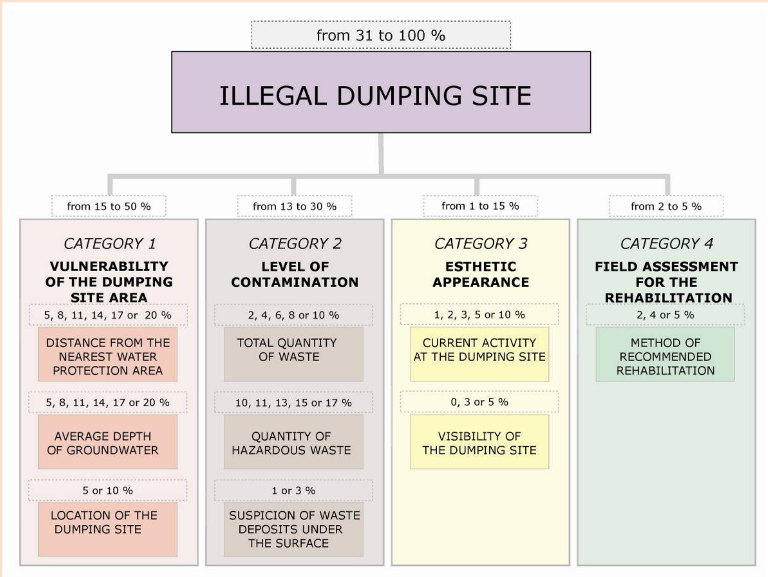


Figure 2.
Classification and evaluation of indicators for establishing priority remediation of illegal dumping sites.

We attributed the greatest weight in the preparation of the priority scale to the vulnerability of the illegal dumping site area; it represents 50 % of the total scale value. Within this category, the primary indicators are the average depth of groundwater and the distance from the boundary of the narrowest water protection area, so converting the percentages directly into weight points we assigned 20 weight points to each of these and the remaining 10 points to the water protection area.

The range of indicators reflecting the properties of the dumping site relative to the level of contamination of the dumping site represents 30 % of the total assessment. The greatest contaminator is hazardous waste or its absolute quantity, to which we have assigned 17 weight points. The total quantity of all waste can contribute 10 points, and a reasonable suspicion that past waste is located beneath the surface of the surroundings of the existing dumping site contributes a further 3 points.We treated the esthetic aspect from the viewpoint that clearly visible and active illegal dumping sites are more problematic because they encourage further illegal dumping. Within this category, to which we have assigned 15 % of the total value in the priority remediation of dumping sites, we have assessed its current activity with 10 points and its visibility with 5 points.

We assigned the smallest percentage in the total assessment to the field estimate of the possibility for rehabilitating the dumping site, assigning it only 5 % of the total assessment due to the subjectivity of the surveyor. A surveyor's subjective opinion about the total danger posed by a particular dumping site, which is based on the characteristics of the dumping site and its distance from a pumping station, is worth considering and assigning weight points to.

The total highest possible number of points obtainable for an individual illegal dumping site is 100; however, the actual values obtained are of course lower (the lowest possible number of points is 29). The round numbers allow a better overview and, relative to the envisaged progression of remediation, the classification of individual dumping sites into priority classes as well as the possible formation of a different number of priority classes.

The points contributed to the total assessment by individual indicators were defined in the following manner:

I. Vulnerability of the dumping site area (50 % of total assessment):

1. Distance from the nearest water protection area (20 %):

Class 1	0 m to 300 m	20 points
Class 2	301 m to 600 m	17 points
Class 3	601 m to 900 m	14 points
Class 4	901 m to 1.200 m	11 points
Class 5	1.201 m to 1.500 m	8 points
Class 6	1.501 m to 1.800 m	5 points

2. Average depth of groundwater (20 %):

Class 1	2.5 m to 4.0 m	20 points
Class 2	4.1 m to 5.0 m	17 points
Class 3	5.1 m to 6.0 m	14 points
Class 4	6.1 m to 7.0 m	11 points
Class 5	7.1 m to 8.0 m	8 points
Class 6	more than 8.0 m	5 points

3. Location in a water protection area (10 %):

Class 1	water protection area I	10 points
Class 2	water protection area IIA	5 points

II. Level of contamination of the dumping site (30% of total assessment):

4. Total amount of waste (10 %):

Class 1	5.001 m^3 to 10.000 m^3	10 points
Class 2	2.001 m^3 to 5.000 m^3	8 points
Class 3	501 m^3 to 2.000 m^3	6 points
Class 4	101 m^3 to 500 m^3	4 points
Class 5	1 m^3 to 100 m^3	2 points

5. Quantity of hazardous waste (17 %):

Class 1	2.001 m^3 to 4.000 m^3	17 points
Class 2	501 m^3 to 2.000 m^3	15 points
Class 3	101 m^3 to 500 m^3	13 points
Class 4	51 m^3 to 100 m^3	11 points
Class 5	1 m^3 to 50 m^3	10 points

6. Reasonable suspicion that past waste is deposited under the surface of the existing dumping site (3 %):

Class 1	reasonable suspicion exists	3 points
Class 2	reasonable suspicion does not exist	1 point

III. Esthetic appearance of the dumping site
(15% of total assessment):

7. Activity of the dumping site (10 %):

Class 1	fully active	10 points
Class 2	partly active	5 points
Class 3	inactive non-overgrown	3 points
Class 4	inactive partly overgrown	2 points
Class 5	inactive overgrown	1 point

8. Visibility of the dumping site (5 %):

Class 1	uncovered	5 points
Class 2	partly covered	3 points
Class 3	covered	0 points

IV. Field assessment of the possibility for the remediation of the dumping site
(5% of On the basis of the characteristics of the dumping site and relative to its distance from the pumping station, the surveyor suggested one of the envisaged recommended methods for the remediation of the dumping site);

9. Method of recommended remediation (5%).

Class 1	complete removal of material	5 points
Class 2	partial removal of material	4 points
Class 3	leveling of material and grassing	2 points

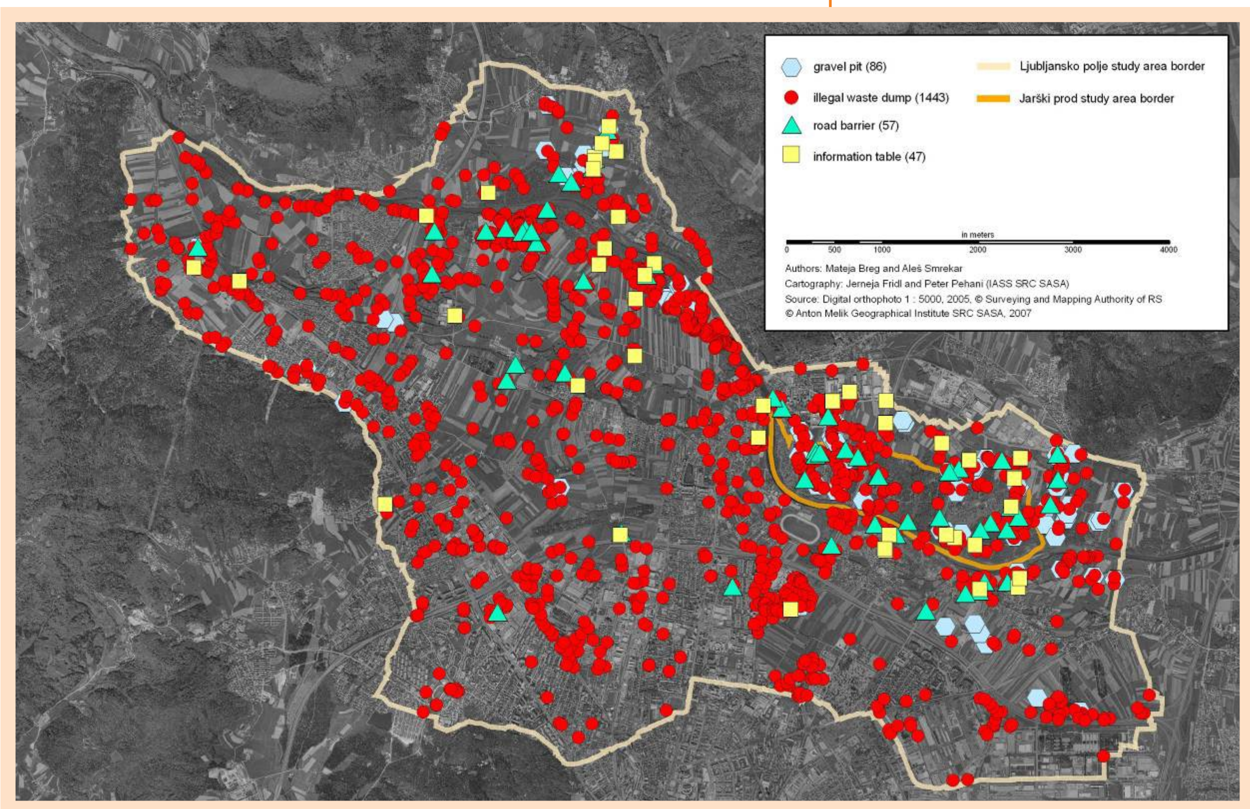
The sum of the points assigned for all nine indicators provided a quantitative assessment of illegal waste dumps with regard to their impact on the water resource and other negative environmental impacts. The dumps were classified into five categories for priority cleanup:

Class 1	from 71 to 90 points
Class 2	from 61 to 70 points
Class 3	from 51 to 60 points
Class 4	from 41 to 50 points
Class 5	from 30 to 40 points

FUNDAMENTAL FEATURES OF THE STUDIED OBJECTS

We found, documented, and studied 1,445 illegal dumping sites on Ljubljansko polje with a total surface area of 120,816 m^2, which means that waste covers 0.28 % of the entire area and makes this one of the most waste-polluted areas in Slovenia. The total volume of the waste is 209,422 m^3. The average dumping site measures 84 m^2 and has 145 m^3 of waste material. We also registered 86 dung pits, 47 information and warning signs, and 57 road barriers on access the roads (Figure 3).

Figure 3.
Surveyed objects.



Size parameters of illegal dumping sites

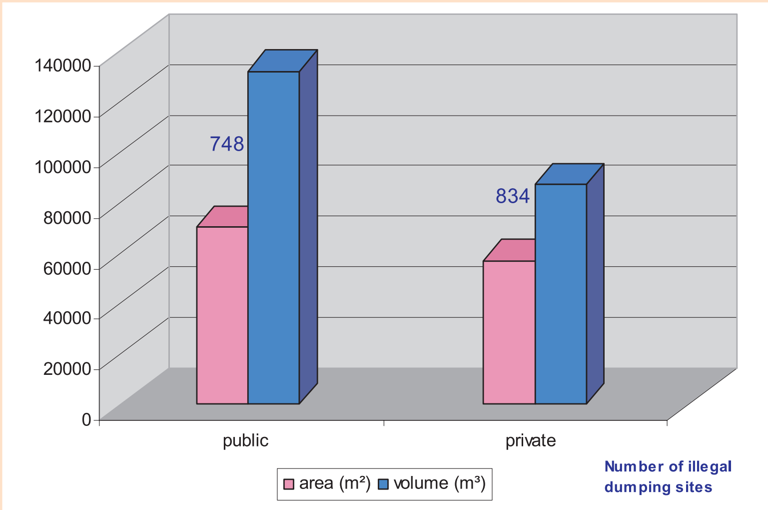
Among the 1,445 surveyed illegal dumping sites, small dumping sites dominate. A good third of the dumping sites do not exceed 10 m^2, and most (696) are in the 11 m^2 to 100 m^2 size class. Only 199 dumping sites measure more than 100 m^2, and only 24 dumping sites exceed 1,000 m^2, which all together occupy 7.3 % of the total surface area of dumping sites. The surface area of the largest dumping site is estimated to be 6,000 m^2.

757 (52.4%) of the dumping sites do not exceed a volume of 10 m^3, but they only contain a small percentage (1.3 %) of the total quantity of the identified waste. On the other hand, there are 36 dumping sites with a volume of 1,000 m^3 and more where almost three quarters of the waste is accumulated. The largest dumping site contains about 42,000 m^3 or almost one fifth of the identified waste.

A minor portion of the waste is located on privately-owned land, while the majority is on “public asset” category land or land owned by legal entities (Figure 4).

Figure 4.

Illegal dumping sites according to land ownership.



On Jarški prod, we studied 151 illegal dumping sites. Forty dumping sites are fully active, 44 partly active, and 67 inactive. We estimate that some 54 dumping sites have existed for less than one year while 97 are apparently older, which indicates still very active waste disposal activities. Their total surface area is 26,273 m^2, which means that the area covered with waste amounts to 1.2 % of the total area. The average dumping site measures 178 m^2.

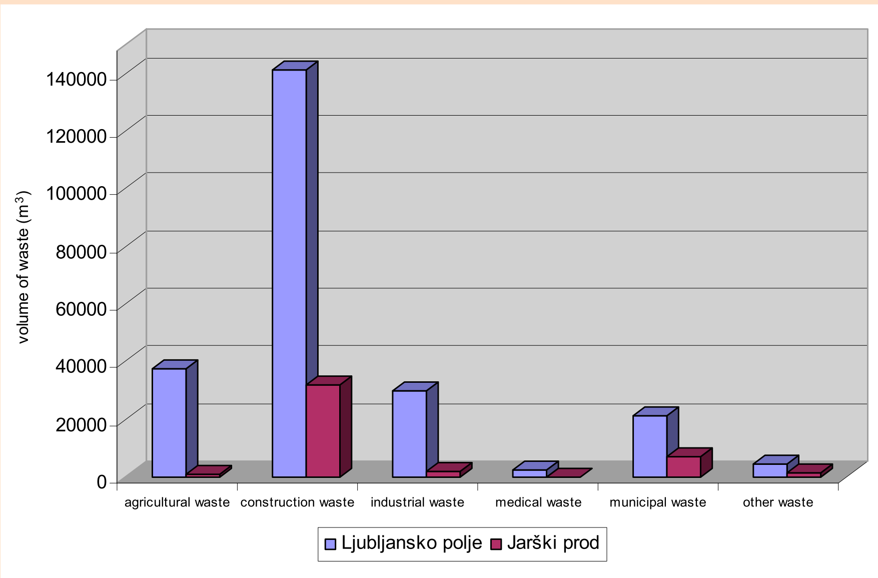


Figure 5.

Volume of deposited waste according to type of waste, comparison of Ljubljansko polje and Jarški prod.

Only thirty are larger than 100 m^2. Four exceed 1,000 m^2, occupying almost six tenths of the total established area of dumping sites. The total volume of the waste is 42,464 m^3.

More than a half of the dumping sites do not exceed 10 m^3, but on the other hand, the six largest dumping sites with volumes of more than 1,000 m^3 have accumulated more than three quarters of all waste.

Composition of waste

Illegally disposed waste is a mix of waste from different sources. Waste from construction and demolition work dominates along with surplus dirt from the excavation of new building sites. There is a great deal of bulky waste: household appliances, furniture, large packaging, electronic devices, vehicles, etc.

In our research, we classified waste into the following groups:

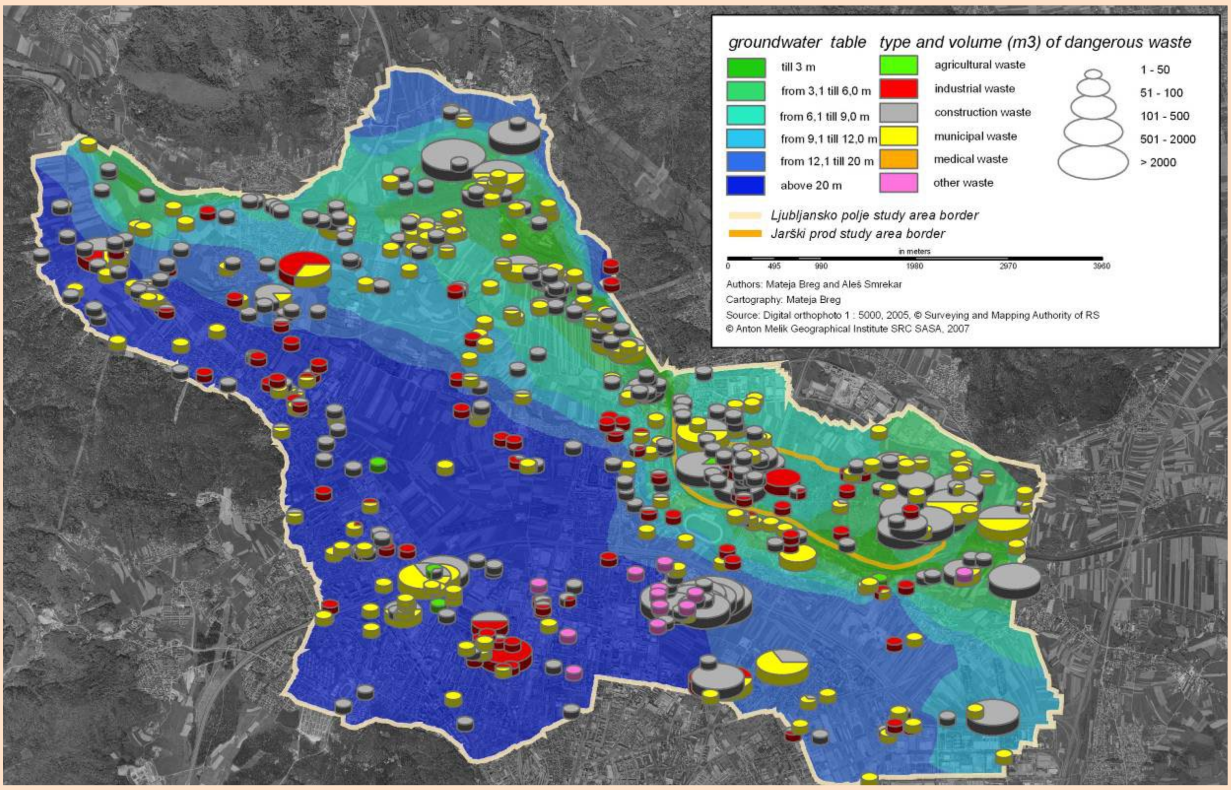
- primary sector waste;
- industrial waste;
- construction waste;
- medical and veterinary waste;
- communal waste;
- other waste.

The results are showed in Figure 5.

The volume of hazardous waste is 28,749 m^3, 13.7 % of the total volume. Hazardous waste is composed mostly of abandoned cars, barrels with unknown contents (empty barrels are classified as bulky waste), and containers for paints, lacquers, motor oils, and agrochemical preparations (Figure 6).

Figure 6.

Spatial distribution of hazardous waste relative to the depth of groundwater.



The main hazardous construction wastes include asbestos panels, asphalt, impregnated glass wool, tar paper, and unemptied containers. Hazardous industrial waste includes parts of machines and devices, the remains of refrigerators, industrial adhesives, paint and solvent containers, paint in plastic bottles, motor oil, and various types of metal barrels with unknown contents. Communal waste includes the remains of household appliances and other appliances containing parts with environmentally-hazardous substances.

Environmental parameters of dumping sites

On Ljubljansko polje, the distance between dumping sites and the surface of the groundwater varies considerably. At about one sixth (15.8 %) of the dumping sites, it measures only three meters, and at a good sixth (17.3 %) between 3.1 and 6.0 meters. At a good fifth (21.8 %), the distance to the groundwater is between 6.1 and 9.0 meters, in just under one tenth (8.4 %) it is between 9.1 and 12.0 meters, and at a good tenth (10.6 %), between 12.1 and 20.0 meters. Almost one quarter (23.6 %) of all illegal dumping sites are located more than 20 meters above the surface of the groundwater.

Waste is scattered everywhere except in the fenced catchment areas. The largest number of dumping sites (760 or 52.6 % of all sites with a total surface area of 57,340 m^2 or 47.5 %, and a volume of 118,975 m^3 or 56.8 %) are located in the narrow areas with a strict water protection regime (IIA). There are only 71 such dumping sites with a total area of 8,589 m^2 (7.2 %) and a volume of 10,249 m^3 (4.9 %).

Most of the illegal dumping sites are located in overgrown areas. On Ljubljansko polje, we registered 87 gravel pits, and only 15 of them were free of waste (Figure 7).

The locations of illegal dumping sites on Jarški prod are typically hidden from view, and according to quantity more than 95 % of the waste material is deposited in thin forest. We discovered 22 of gravel pits. Their surface area ranges from 25 m^2 to 65,000 m^2, their volume is between 50

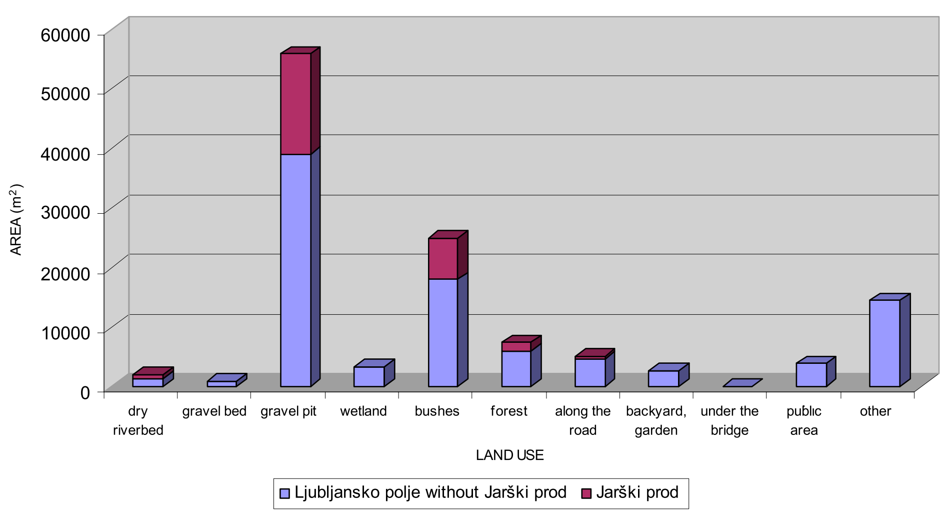


Figure 7.

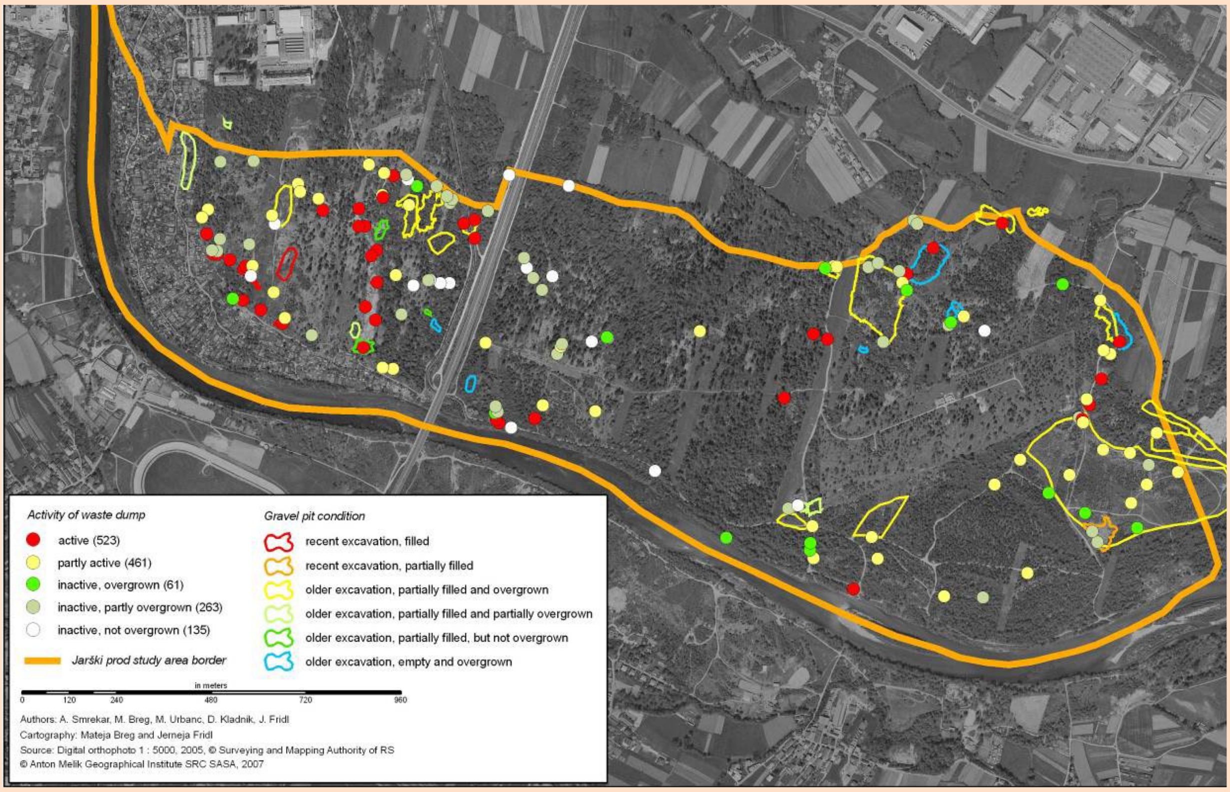
Area of illegal dumping sites according to land use.

m^3 and 130,000 m^3, and they are up to six meters deep. The average gravel pit measures 8,550 m^2 and has a volume of 22,042 m^3. Only 38 dumping sites were actually found in gravel pits, but they contained as much as 31,732 m^3 or almost three quarters of all the recorded waste.

More than a third (36.2 %) of the dumping sites are still active, just under one third shares go to both partly active and inactive illegal dumping sites. Most (263) of the inactive dumping sites are partly overgrown. Considering the quantity of the waste with more than a half share (51.4 %), inactive dumping sites are in the lead, while fully active dumping sites contribute just under a third (30.9 %) (Figure 8).

Figure 8.

The relationship between the condition of gravel pits and the activity of dumping sites on Jarški prod.



There is reasonable suspicion that additional quantities of past waste are deposited under the surface on 359 dumping sites (24.8 %). Unfortunately, this suspicion applies especially at the major dumping sites where we registered 87,009 m^3 or 41.5 % of the total quantity of waste. More than two thirds (67.5 %) of illegal dumping sites are located less than five meters from access roads.

Various types of roads lead to dumping sites. The most common are wagon tracks (491 dumping sites or 24.6 % from the area aspect and 22.6 % from the quantity of waste aspect), followed by dirt roads (364; 59.4 % or 67.6 %) and asphalt roads (340; 10.9 % or 7.7 %). Only a small amount of waste was brought to dumping sites via footpaths (119; 2.7 % or 1.4 %). Similar figures (131; 2.4 % or 1.4 %) apply to dumping sites with no access roads.

Various types of barriers set up on asphalt and dirt roads, as well as on wagon tracks and footpaths, should be the largest hindrance to unobstructed delivery of waste material. Unfortunately, it is possible to get around them in many cases. An interesting fact is that 222 dumping sites with 42.9 % of the total surface area and 55.0 % of the total volume are only accessible by passing road barriers, however, new piles of waste have started to accumulate before the barriers.

RESULTS AND DISCUSSION

Results of analyses of waste deposits relative to limit values

The locations and results of analyses of waste disposed on individual larger illegal dumping sites of Ljubljansko polje and Jarški prod are presented in Figure 9 and Table 2. The samples differ in a number of ways. Samples from the entire Ljubljansko polje are more heterogeneous, moister, and contain more organic substances. Both contain more organic substances than allowed for disposal on inert waste dumping sites or input into the ground. Standard leachates from waste show moderate contamination, but some parameters exceed the limit values for inert waste or waste that can be deposited into the ground as artificially prepared soil. It was concluded that the main potential contribution of the waste to the pollution of the environment is contamination with organic substances of biological and synthetic origin that occur during the spontaneous decomposition of waste in a natural environment.

We analyzed the leachate of an average sample from Jarški prod for potential organic contaminants: polycyclic aromatic hydrocarbons (PAO), absorbent organic chlorine (AOX), lower aromatic hydrocarbons (BTEX), and polychlorinated biphenyls (PCB). The established amounts are well

Figure 9.
Locations of soil sampling on Ljubljansko polje.

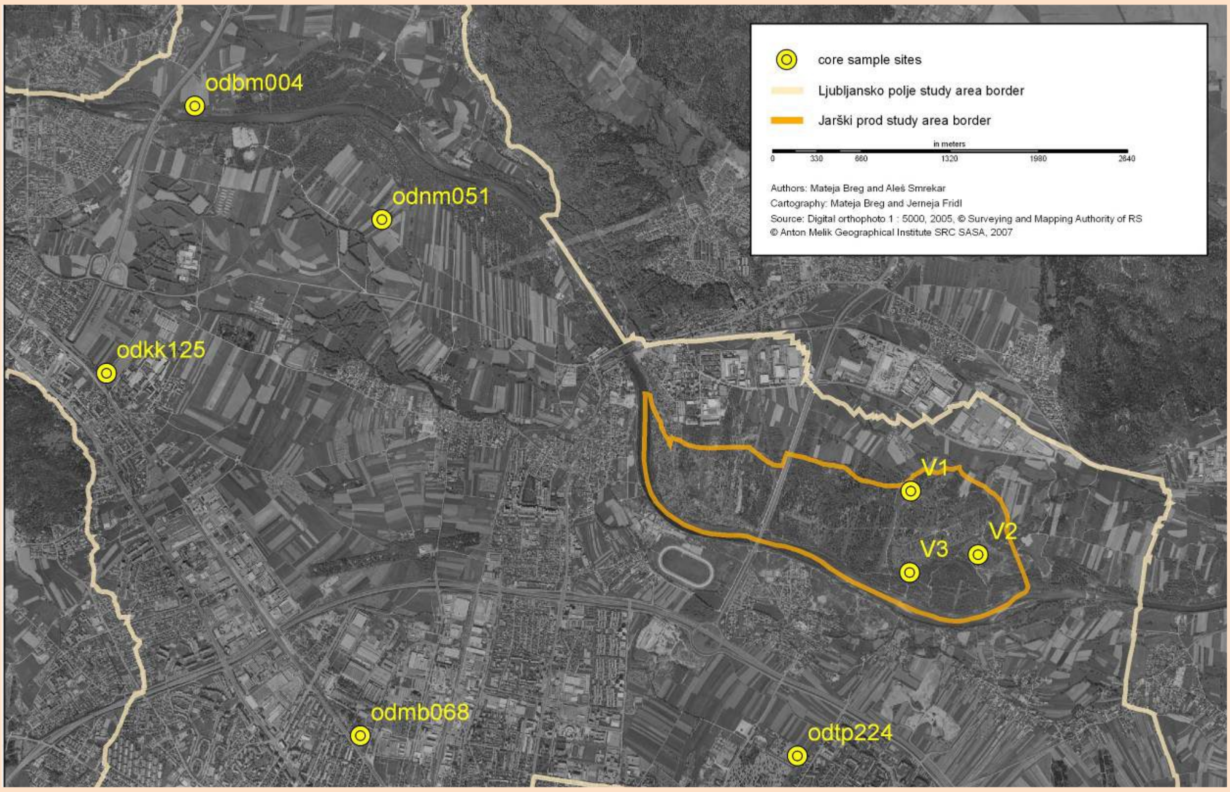


Table 2.
Results of analyses of deposited waste in comparison with limit values.

Waste properties	Method of determination	Unit	Measured values Ljubljansko polje (5 samples)		Measured values Jarški prod (3 samples)		Limit values Regulations for Waste Disposal			
			Waste samples	Standard leachate	Waste samples	Standard leachate	IW	NHWLLOS	NHWHLOS	Soil contamination APS
dried remains (105 °C)	SIST EN 12880	%	76.1-99.0		92.2-93.9		-		-	-
ash (550°C)	SIST EN 12879	% DS	7.8-17.0		1.4-1.8		-	5	-	-
total organic carbon –TOC	SIST ISO 10693	% C DS	3.85-11.12		0.3–5.0		3	3	18	0,3
pH	SIST ISO 10523	/		7.4 - 8.3		7.1-8.1	-	-	-	6.5-8
total soluble substances	SIST EN 12880	g/kg DS		1.0 - 23.5		0.17-0.29	4	60	60	-
DOC	ISO 8245	mg/kg DS		170 - 946		90-102	500	800	7500	50
antimony	ICP MS	mg/kg DS		< 0.06		< 0.7	0,06	0,7	0,7	-
arsenic	ICP MS	mg/kg DS		< 0.1		< 1	0,5	2	2	20
copper	ICP AES	mg/kg DS		< 20		< 1	2	50	5	30
barium	ICP AES	mg/kg DS		< 20		< 1	20	100	100	-
zinc	ICP AES	mg/kg DS		< 40		< 1	4	50	50	100
cadmium	ICP MS	mg/kg DS		< 0.04		< 0.1	0,04	3	1	0,5
total chromium	ICP AES	mg/kg DS		< 5		< 1	0,5	10	10	40
molybdenum	ICP AES	mg/kg DS		< 5		< 1	0,5	10	10	-
nickel	ICP AES	mg/kg DS		< 4		< 1	0.4	10	10	30
lead	ICP AES	mg/kg DS		< 5		< 1	0.5	10	10	40
selenium	ICP AES	mg/kg DS		< 0.1		-	0.1	0.5	0.5	-
mercury	ICP MS	mg/kg DS		< 0.01		< 0.1	0.01	0.2	0.2	0.2

IW = inert waste, NHWLLOS = non-hazardous waste with low level of organic substances, NHWHLOS = non-hazardous waste with high level of organic substances, DS = dry solids, APS = artificially prepared soil intended for landfill.

under the permissible values. This type of chemical pollution from deposited waste is therefore minor, which was to be expected.

The influence of illegal waste dumps on the groundwater quality of Ljubljansko polje

Despite the numerous illegal waste dumps on the catchment areas of drinking water wells, the national groundwater quality monitoring service and the city's drinking water supplier have not confirmed unequivocally the existence of contaminants in the groundwater originating from waste dumps. This is probably due to the following reasons:

• The groundwater flow in the central part of the aquifer is locally relatively high. For example, it was determined that the velocity reached 20 m/day locally [16]. Consequently, a contaminant possibly present in the groundwater is dissolved and removed relatively quickly from the aquifer by natural processes of dispersion, dilution, and biodegradation (in the cases of biodegradable substances).

• The quality of water in the immediate catchment areas of the pumping stations is not monitored and tested frequently. It is therefore possible that the wave of a contaminant moves with the groundwater flow in the period of the year when the groundwater is not sampled.

• A point source contaminant in the Ljubljansko polje aquifer travels within a relatively narrow zone and does not disperse over the wider area. The contaminant can be detected at the sampling sites only if the sampling site is situated in the contaminant's path, which usually does not exceed more than a few dozen meters and depends on the distance of the source point.

• It is possible that a contaminant detected at a particular sampling site originated from an illegal waste dump (e.g., pesticides, volatile organic hydrocarbons) but the researcher assumes it comes from agricultural or household use.

Table 3.
Results of tests of drinking water at the Kleče pumping station in 2005 and 2006.

Parameter	Units	Max. admissible value	Kleče-12 (19.4.05)	Kleče-12 (8.5.06)
Electroconductivity	μS/cm	2500	523	489
Nitrates	mg/l $N\text{-}NO_3$	50	17.0	15.2
Nitrites	mg/l $N\text{-}NO_2$	0.5	<0.001	<0.001
TOC	mg/l C	/	<0.2	1.1
Atrazine	μg/l	0.1	0.0572	0.0343
Desethylatrazine	μg/l	0.1	0.0781	0.0607
Chromium	μg/l Cr^{+6}	50	4	<3
Tri- and Tetra –chloroethylene (sum)	μg/l	10	0.08	0.16

Table 4.
Results of tests of drinking water at the Šentvid pumping station in 2005 and 2006.

Parameter	Units	Max. admissible value	Šentvid-1a (20.4.05)	Šentvid-1a (8.5.06)
Electroconductivity	μS/cm	2500	558	582
Nitrates	mg/l $N\text{-}NO_3$	50	19.0	19.4
Nitrites	mg/l $N\text{-}NO_2$	0.5	<0.001	<0.001
TOC	mg/l C	/	<0.2	0.45
Atrazine	μg/l	0.1	0.0246	0.0225
Desethylatrazine	μg/l	0.1	0.0447	0.0412
Chromium	μg/l Cr^{+6}	50	<3	<3
Tri- and Tetra –chloroethylene (sum)	μg/l	10	<0.06	<0.06

Table 5.
Results of tests of drinking water at the Jarški prod pumping station in 2005 and 2006.

Parameter	Units	Max. admissible value	Jarški prod-3 (20.4.05)	Jarški prod-3 (8.5.06)
Electroconductivity	μS/cm	2500	521	533
Nitrates	mg/l $N\text{-}NO_3$	50	11.0	11.2
Nitrites	mg/l $N\text{-}NO_2$	0.5	<0.001	<0.001
TOC	mg/l C	/	<0.2	0.58
Atrazine	μg/l	0.1	0.0079	0.0069
Desethylatrazine	μg/l	0.1	0.0206	0.0237
Chromium	μg/l Cr^{+6}	50	<3	<3
Tri- and Tetra –chloroethylene (sum)	μg/l	10	0.2	0.2

• The scope of the chemical analyses is limited and can neither quantitatively nor qualitatively include all the substances from the anthropogenic environment.

• Finally, the illegal waste dumps are not such important sources of contaminants as has been assumed.

In dealing with the groundwater quality problems of the Ljubljansko polje aquifer, in addition to the traces of pesticides the traces of volatile organic hydrocarbons (e.g. trichloroethylene (TCE) and tetrachloroethylene) and heavy metals (e.g. chromium) should be discussed. The test results show that the concentrations of contaminants in the drinking water are low and that their presence is not harmful for users. While the previous usage of pesticides in the agriculture is definitely one of their origins in the groundwater, the reasons for the presence of the volatile organic hydrocarbons that have been detected in traces all over the area are not well known and understood. In addition to the dispersed usage of volatile organic solvents in households and industry, the waste dumps could have been one of the sources of volatile organic hydrocarbons in the groundwater of Ljubljansko polje but no research has been done to prove this assumption. Tables 3, 4 and 5 shows main results of the tests of drinking water at selected active wells of the public water supply system in 2005 and 2006.

The results of the drinking water tests confirm that the drinking water in Ljubljana's public water system does not contain contaminants in the concentration range that could make the water undrinkable.

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PRIORITY REMEDIATION OF ILLEGAL DUMPING SITES

In the long run, the cost for the periodic remediation of larger dumping sites is higher than for regular material collection from minor dumping sites, although this only applies when such a system is already established [9]. In time, it will be necessary to rehabilitate all illegal dumping sites; however, due to the large quantity of waste it is unrealistic to expect this to happen in one go. Using the described evaluation methodology for each illegal dumping site, we calculated the total number of points, which reflects the assessment of all of the nine considered indicators given their weighted values (Figure 10).

Due to the substantial weight of the vulnerability of the dumping site area category, which contributes half of all possible points, the 58 illegal dumping sites ranked in priority class 1 with 71 to 93 points (of the theoretically possible 100) are on the majority of the surveyed areas located in the vicinity of pumping stations. This is particularly characteristic for the area of the Jarški prod pumping station.

218 illegal dumping sites (15.1 % of all) obtained between 61 and 70 points and were ranked in priority class 2. On Ljubljansko polje, they are concentrated particularly in four areas, with most located on Jarški prod. There are also major concentrations on the right bank of the Sava River between Jarše and Sneberje, north of Kleče, and southwest of Hrastje.

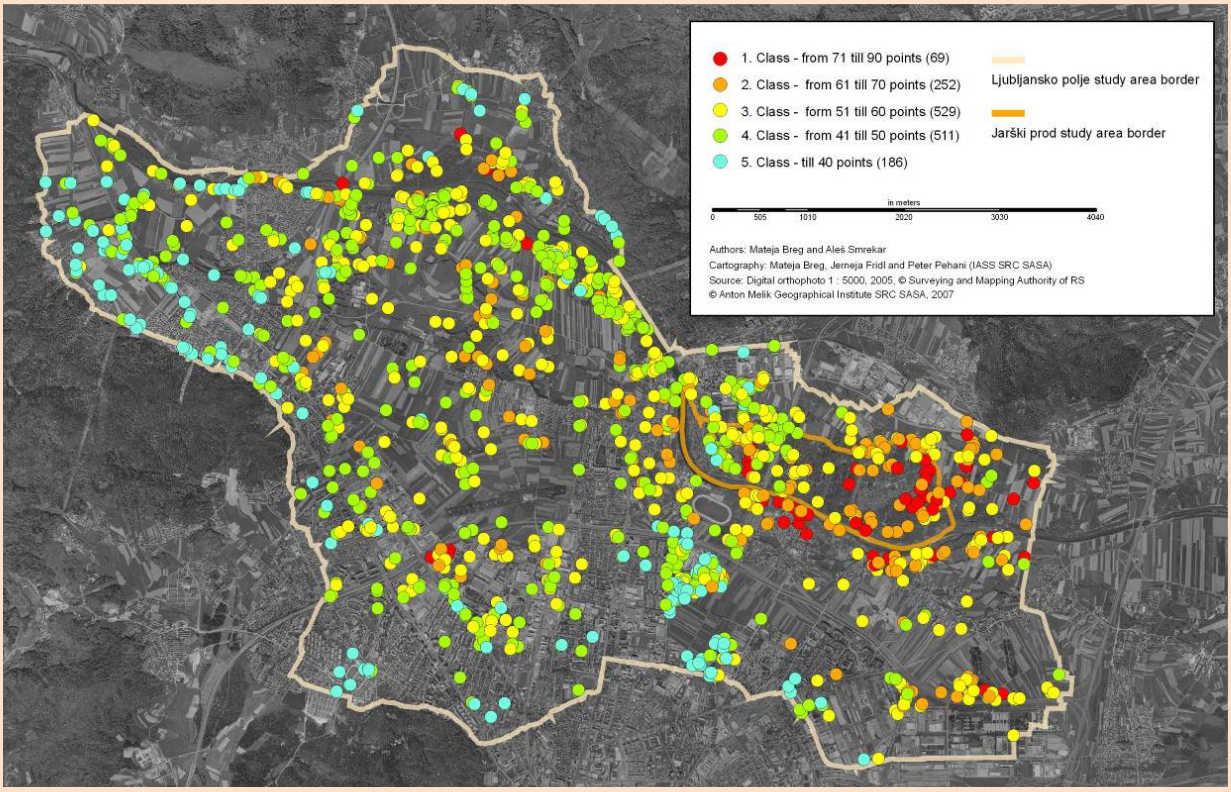

Figure 10.
Priority remediation of illegal dumping sites.

Dumping sites in priority class 3 with 51 to 60 points, in which 491 (34.0 %) of the illegal dumping sites are ranked, are scattered over all of the surveyed areas in no particular pattern. 493 (34.1 %) illegal dumping sites are ranked in priority class 4 with 41 to 50 points. These too are quite evenly distributed, there are fewer in the vicinity of pumping stations of Jarški prod and Hrastje.

Priority class 5 contains 183 illegal dumping sites with less than 40 points (the lowest possible number is 26). They are not placed in the vicinity of the pumping stations, and since their waste is not very hazardous, the need for their remediation is the smallest.

According to the results the selected methodology, it has been concluded that the majority of illegal dumping sites that require immediate remediation (class 1 and 2) which are located in water protection areas I or in their immediate vicinity where the regulations protecting the water resource for the supply of Ljubljana with drinking water are very strict.

Revitalization of the degraded landscape is only possible by employing high quality remediation programs. These require a precise assessment of the existing excessive contamination of the environment and a weighted selection of the most suitable methods and measures to improve the situation. Therefore their implementation demand a special approach according to the Article 56 of the Environmental Protection Act [29].

Next important activity is to prevent further dumping. Road blocks should be set up on access roads leading to the most critical areas. The problem can only be solved permanently through regular monitoring, a system of penalties, and raising the awareness of people who are potential polluters.

Southeast of the Jarški prod pumping station there are a number of illegal dumping sites ranked in class 1 and 2 according to the criteria for the priority remediation of dumping sites that are still active and therefore encouraging further dumping. Dumping attempts could be prevented or at least substantially reduced by simply erecting two gates on the more important access roads north and southwest of this already distinctly degraded area of former large gravel pits. A gate should also be erected on the southern access to this area. The second area that demands immediate protection is the gravel pit site west of Štajerska cesta that has supplied gravel and sand as construction material since 1995.

CONCLUSION

Despite the relatively low concentration of contaminant that could originate from the illegal waste dumps, it can be assumed that every single location where waste is illegally deposited represents a serious threat to the groundwater and the quality of drinking water, since even a small quantity of contaminant can make the water resource undrinkable. The results of research that do not confirm the frequent occurrence of groundwater contamination from waste dumps should not be a reason to neglect the problems related to illegal waste dumps. Beside that also the landscape and ecological characteristics with the emphasis on other negative impacts (specially visual, aesthetic and functional) of illegal dumping sites should be considered.

Solving the problem of illegal dumping sites requires two simultaneous approaches. The first is to rehabilitate existing dumping sites and thus remove point sources and larger plane sources of contaminators of the underground water, and the second is to effectively prevent the occurrence of new dumping sites, strictly penalize violators, and organize campaigns to raise environmental awareness.

So far, there has not been enough will – and consequently funds - to resolve this problem. Recently, however, the city authorities have apparently realized the need to take action, shown by the fact that in addition to the waste collection carried out by Snaga the first more comprehensive steps have been taken. A remediation project for the most polluted area of Jarški prod is in the preparation phase, which will be followed by a test implementation of the remediation.

To successfully implement the established goals of waste management, it is necessary to inform, educate, and raise awareness. Endeavours without the support and appropriate level of environmental awareness of the local population will not achieve the goal, a clean and healthy local landscape. It is obvious that a non-problematic environment does not represent a value for many people.

To successfully implement the established goals of waste management, it is necessary to inform, educate, and raise awareness.

The Spatial Plan of the City Municipality of Ljubljana [30] envisages this area as a forest area with accented ecological and recreational significance. A system of walking and cycling paths could be arranged along the Sava River that with the appropriate remediation would give the area new quality dimensions. There are ideal possibilities here for a water education trail where various items and topics could be presented such as the operation of pumping stations, the dry riverbed of a former watercourse, the regulation of a riverbed, a gravel pit with a profile of the cover layer and gravel on an alluvial plain as an inappropriate source of construction material, and an illegal dumping site as an inappropriate use of a gravel pit just above the groundwater table, etc.

These and other endeavours at the level of the City Municipality of Ljubljana have been undertaken particularly by the Institute for Nature Conservation of the Republic of Slovenia. One of its missions is to publish information and motivation publications such as Environment in the City Municipality of Ljubljana [31] and A Guide to the Protection of Underground Water in the City Municipality of Ljubljana [32].

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Original scientific paper

Removal of Cu, Cd, Zn, Ni and Fe from wastewater comparison of three different substrates used in model scaled constructed wetland

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ABSTRACT:

Different wastewaters contain metals that, unlike organic pollutants, are not degradable in the biological treatment system. Primary removal mechanisms can be achieved via sorption with a use of effective sorption media and precipitation processes which have been well demonstrated for metal removal also in wetland environment.

The aim of the study was to test substrates like sand, peat and ceramics waste particles for removal of selected metal ions in a model-scaled constructed wetland (CW). The model comprised three large compartments where sand, peat-sand mixture or ceramics waste particles were exchanged in three successive experiments.

In the compartment filled with sand 99.3 %, 97.8 %, 97.8 %, 97.0 %, and 32.2 % efficiency of metal removal for Cu, Cd, Pb, Zn, and Ni was achieved respectively. Fe leached out of the substrate in this experiment. In the compartment filled with the mixture of peat and sand was the efficiency of metal removal for Zn 99.8 %, Cu 99.3 %, Cd 98.0 %, Pb 97.9 %, Ni 95.8 %, and Fe 28.3 %, while in the compartment with ceramics the treatment efficiency reached for Cu 99.6 %, Pb 98.0 %, Cd 98.0 %, Fe 92.8 %, Zn 52.0 %, and for Ni 12.4 %. The substrates used in horizontal subsurface flow model expressed the capacity of efficient metal reduction from wastewater and indicate on the possibility of their application in a real-scale CW as a separate, cost-efficient pre-treatment or post-treatment step in the case of additional need of metal removal from the wastewater.

KEY WORDS:

Constructed wetland, Sand, Peat, Ceramics, Heavy metal, Substrate, Wastewater treatment

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INTRODUCTION

Toxic metals pose a serious threat to the fauna and flora of receiving water. In spite of strict regulations restraining the careless disposal of metal ions, they still emerge in a variety of wastewaters like road runoff, landfill leachate, mine drainage and in the specific industrial runoff (processing, surface treatment like galvanization) [1,2,3]. The common methods for removal of low concentration of metals from wastewaters are either economically unfavourable (e.g., conventional ion exchange, electrolytic or liquid extraction, electrodialysis) or technically complicated (e.g. precipitation, cementation, reverse osmosis) [4]. The cost of adsorptive metal removal process is relatively high when pure sorbents (activated carbon or hydrated oxides) are used [5]. Therefore, there is an increasing trend of substituting pure adsorbents with natural by-products or stabilised solid waste materials. Especially in developing countries, there exists a great need to use low-cost materials in wastewater treatment processes [6]. Recent developments use in situ treatment of metal contaminated soil and water like electrokinetics, phytoremediation, bioprecipitation processes, soil flushing, solidification and stabilization. In general, in situ remedies are often more economically efficient compared with traditional treatment methods.

The aim of this study was to test substrates like sand, peat and waste ceramics particles for metal ions removal from contaminated water in model scale plant used as a base for application in constructed wetland (CW). If successful, these substrates could provide a cost effective alternative. CWs are already widely used in treating different types of wastewater, such as sewage, storm water, highway runoff, industrial wastewater, agricultural runoff, acid mine drainage and landfill leachate [1,5,7,8,9,10,11,12,13,14]. They are ecosystems, which can be successfully manipulated to treat wastewater. Furthermore, when harnessed, the biological, chemical and physical processes that occur in these ecosystems can be beneficial low cost option for civil applications. They are well suited for large volumes of wastewater with low concentrations of metals. The mechanisms for metal removal in wetlands include beside sedimentation a number of other processes that may be significant including filtration by plants, adsorption, biological assimilation, chemical transpiration and volatilization [2,15]. Experiences in the beginning period of CW operation with too low or too high hydraulic permeability showed that the substrate is of key importance in achieving efficient treatment [16]. However, the substrate represents a major expense at the CW construction. In a case of a need of a frequent substrate exchange, or for the purpose of the removal of specific pollutants, like metal ions, the selection of efficient and cost-effective substrate is very important. For the presented study metal removal efficiency was tested in a model-scaled CW filled with different substrates and inoculated with indigenous microbes, without planting with macrophytes. The main objective of the study was to evaluate the efficiency of three pre-selected materials under controlled experimental conditions to identify the most promising for the potential use in the wastewater treatment with the use of CW. Out of a wide range of sorbents which are available as possible filtration media, sand, peat

Experiences in the beginning period of CW operation with too low or too high hydraulic permeability showed that the substrate is of key importance in achieving efficient treatment.

and ceramics were selected on the basis of market accessibility and pre-experiment work completed.

This study follows the simultaneous removal of six different metal ions: Fe, Zn, Cd, Ni, Pb, and Cu as dissolved fractions of these metals often pose environmental concern and were found also in preliminary performed analysis of leachate, highway runoff and industrial wastewater [1,14]. Ni is a naturally occurring element that may exist in various mineral forms. It is used in a variety of applications, including metallurgical and electrical components, such as batteries. Like most metals, the toxicity of Ni depends on the route of exposure and the solubility of Ni compounds [17]. Pb is a natural element, persistent in water and soil. Most Pb in the environment is from anthropogenic sources [18]. Zn is used primarily in galvanized metals and metal alloys, but Zn compounds have also wide commercial applications [19]. Fe is an active metal. It combines with halogens, sulphur, phosphorus, carbon and silicon, and it displaces hydrogen from most dilute acids. Toxicity of Fe to plants is rare, but may occur primarily on acid soils (pH <5.0). Cd occurs predominately in the form of free divalent cations in most well-oxygenated, low-organic-matter and freshwaters [20]. However, particulate matter and dissolved organic matter can bind Cd in biologically unavailable forms. Aquatic organisms are able to bioaccumulate Cd. Cd is a highly toxic metal with no known nutrient properties. It is toxic to a variety of mechanisms in numerous tissues. Cu occurs in natural waters primarily as a divalent cupric ion in free and complexed forms [20]. Cu is a micro nutrient for both plants and animals at low concentrations, but at concentrations only slightly higher, it is toxic to aquatic life. The largest anthropogenic releases of Cu into the environment result from mining operations, agriculture, solid waste and sludge from sewage treatment plants.

METHODS

A model-scaled wetland – 58.5 cm high, 30 cm wide, with the bottom length of 299 cm and the upper length of 316 cm, without vegetation was placed in an unheated laboratory hall (Figure 1). The measured

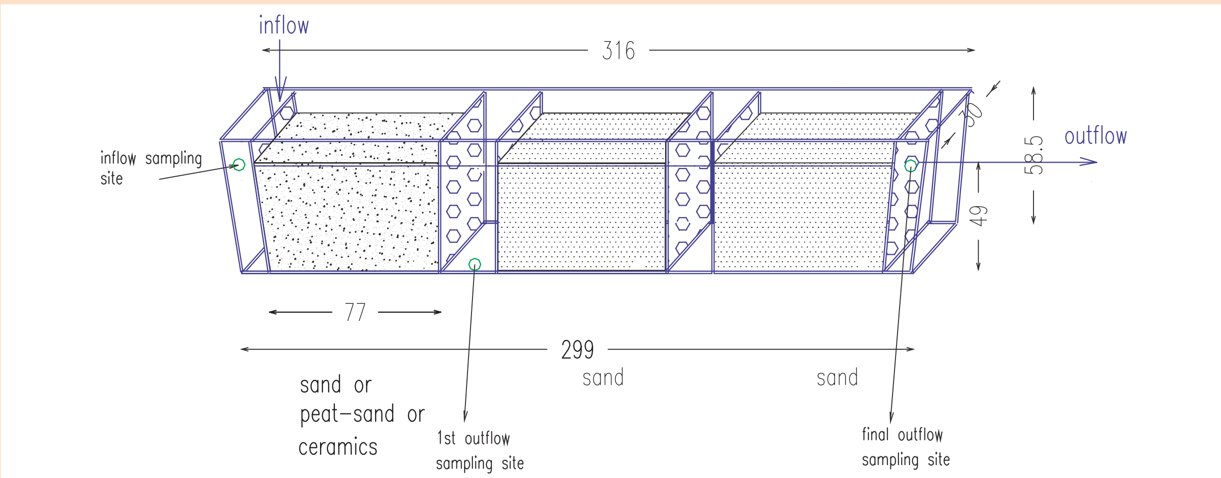

Figure 1.
The model-scaled wetland divided into seven compartments, filled with sand, peat and ceramics particles.

daytime temperature range was between 6.9 °C and 20.6 °C through the experiment, following the external environmental conditions. The model was divided into seven compartments, separated by six perforated walls. Three large compartments (77 cm long) were filled with substrate up to 49 cm.

Three successive experiments were carried out. In all three experiments, the last two compartments were filled with sand (1 mm – 4 mm diameter size). In the first compartment, sand (Experiment A: sand/sand/sand), peat-sand mixture (Experiment B: peat-sand/sand/sand) and ceramics (Experiment C: ceramics/sand/sand) were exchanged in each experiment. Small compartments (20 cm – 25 cm) were not filled with substrate in order to carry out the sampling for water analyses.

Sand was included for three main reasons. Sand is frequently used substrate in CW so the current study can provide data for comparison with other two substrates, as well as sand filtration has been commonly used for storm water filtration, with similar characteristics as prepared water in our case (low BOD5 content and presence of metal ions). Washed sand (1 mm – 4 mm diameter size) was obtained from a gravel pit Hotič, Slovenia.

Peat was used on the basis of obtained results from leachate treatment in CW, where higher treatment efficiency had been achieved with additions of peat to the sand substrate compared to treatment beds filled only with sand substrate [8]. Additionally, peat was chosen as an organic material with different natural properties than sand and ceramics, with high cation exchange and sorption capacity.

Before the start of each experiment, sewage with water addition (1:1) was run through the model for seven days to establish the bacterial population in the fresh substrate, to simulate conditions in CW treating sewage.

Sphagnum peat, prepared for horticultural application, without additions of fertilizers or lime, with pH ranged between 4.0 – 4.5 and fibre size between 0 mm – 200 mm was used in a mass ratio 1:3 mixture with sand.

Ceramics was selected as an economically accessible substrate, as waste particles from the ceramics production were used, obtained from the ceramics works Keramika Liboje. Waste porous ceramics particles (size of pore 0.2 μm) were broken by hand into small pieces (1 mm – 8 mm) and washed to eliminate finer material.

Before the start of each experiment, sewage with water addition (1:1) was run through the model for seven days to establish the bacterial population in the fresh substrate, to simulate conditions in CW treating sewage. The dilution was made in order to avoid clogging in the substrate. After substrate inoculation with indigenous micro flora from sewage, prepared artificial wastewater polluted by metals was run through the model for five days in each experimental case. The required concentrations of Cu, Ni, Pb, Zn, Fe and Cd were obtained by step-by-step diluting their commercial stock solutions at 1000 mg/L in HNO^{3} to the desired concentrations of 2.5 mg/L for Cu, Ni and Pb; 10 mg/L for Zn and Fe, and 0.5 mg/L for Cd. As a bacterial nutrient source sugar was added in 1 % concentration. The artificial wastewater was supplied with 0.1 L/min flow from a 200 L container positioned above the inflow level into the model enabling gravitational flow through the model. Figure 1 shows the inflow and the outflow positions in the model and the sampling points. The water flow in the model was sub superficial.

An analysis of physical and chemical parameters in sewage of the pre-experimental stages and in prepared artificial wastewater were performed. Before the start of each experiment, a sample of sewage was taken at the final outflow of the model for the analyses of metal content, temperature, pH, dissolved oxygen and specific electric conductivity (G). Samples for the same analyses of artificial wastewater were ta ken at the inflow, and during five days of the experiment at the outflow from the first compartment (first outflow) and at the final outflow from the model (Figure 1) during each experiment. Temperature, pH, G and oxygen content were measured on site, using the MultiLine P4 portable universal pocket-sized meter with the pH combined electrode, SenTix 41 integrated temperature probe, CellOx 325 dissolved oxygen probe and TetraCon 325 standard conductivity cell. Samples for metal analyses were collected in plastic bottles and frozen. 1 mL suprapur HNO^3 per 1 L of sample was added immediately after sampling. Before the analyses, the samples were thawed to room temperature and filtered through white ribbon. All analyses were performed with flame atomic adsorption spectrometry (FAAS), Varian Specter AA 110 (Mulgrave, Victoria, Australia). Cu, Zn, Cd and Pb were determined in the air-acetylene flame, whereas Fe and Ni in the N2O-acetylene flame. Standard solutions were prepared from stock standard Cu, Ni, Fe, Cd, Zn and Pb solutions in the concentration of 1,000 ± 2 mg/L (Merck, Darmstradt, Germany).

At neutral pH we can expect mainly the processes like adsorption of metals, chelate formation and ion exchange on the chosen substrate.

RESULTS AND DISCUSSION

During five-day flow of artificial wastewater in all three experiments, pH ranged between 6.5 and 7.8 (Table 1). Compared to the inflow values, a slight decrease in 0.5 – 1 pH was noticed at both outflows in all three experiments. The decrease of pH could be due to microbial degradation of organic matter in anoxic conditions. The decrease could be in part due to the exchange of metal ions for hydrogen ions on the substrate surface. Eger [3] reported a decrease of about 0.1–0.2 pH units at the outflow after the flow of mine drainage through the wetland treatment cell filled with peat substrate. In general, CWs have buffering capacities, which means that the outflow pH remains in the range of neutral limits irrespective of the inflow pH [16]. A similar situation was found in our model where the average pH was 7. At neutral pH we can expect mainly the processes like adsorption of metals, chelate formation and ion exchange on the chosen substrate [3].

There were distinctive differences found in the concentration of dissolved oxygen in the model comparing inflow and outflow tares (Table 1). At the beginning of the artificial wastewater flow, the concentration of dissolved oxygen in the inflow compartment was high (7.9 mg/L on average) and it immediately dropped after the percolation through the first compartment filled with the substrate and stabilized in the other parts of the model at 1.0 mg/L on average. Dissolved oxygen from the inflow water was imme-

Table 1.

Parameters measured at the outflow during pre-experimental stage with sewage (Sewage) and in the prepared artificial wastewater at the beginning (Inflow) and during five days of water percolation through the model (1st outflow, Final outflow) of each experiment.

EXPERIMENT A

Parameter	Unit	Sewage	Inflow	1st outflow	Final outflow
Temperature	°C	16	17	17.5	17.4
pH		7.8	7.5	6.5	6.7
Dissolved oxygen (O_2)	mg/L	1.63	6.4	1.37	1.05
G	μScm	626	310	646	662

EXPERIMENT B

Parameter	Unit	Sewage	Inflow	1st outflow	Final outflow
Temperature	°C	13	11.9	8.8	6.9
pH		7.4	7.2	6.5	6.7
Dissolved oxygen (O_2)	mg/L	0.81	8.41	1.34	0.56
G	μScm	1177	490	1711	1793

EXPERIMENT C

Parameter	Unit	Sewage	Inflow	1st outflow	Final outflow
Temperature	°C	18.2	18.1	20.5	20.6
pH		7.5	7.3	6.7	6.7
Dissolved oxygen (O_2)	mg/L	2.89	8.94	1.02	0.85
G	μScm	822	457	539	1740

diately incorporated into the degradation processes. Similar low concentration of dissolved oxygen could be found in water at the outflow from CW with horizontal subsurface water flow [16].

The inflow specific electric conductivity (G) of prepared artificial wastewater ranged between 310 μS/cm and 490 μS/cm (Table 1). Upon the percolation of artificial wastewater through the substrate, the G increased in all three experiments and it ranged between 539 μS/cm and 1,793 μS/cm at the outflows. A positive correlation was found between higher G and leaching of Fe ions from the sand substrate.

Before the beginning of each experiment, the concentration of metal ions was analysed at the outflow during sewage flow through the model in the pre-experimantal stage of each experiment. The results are presented in Table 2. Figure 2 represents the concentrations of metal ions in prepared wastewater at the inflow and at the first and final outflow from the model after five days of artificial wastewater percolation through the model in each experiment. The efficiency of Cu removal was very high in all three tested substrates already in the first compartment (sand 99.3 %, peat-soil mixture 99.3 %, ceramics 99.6 %). In

Table 2.

Concentration of metals present in sewage of the pre-experimental stage expressed in mg/L.

Experiment	Cu	Zn	Cd	Ni	Pb	Fe
A	0.053	0.328	<0.01	0.119	<0.05	1.69
B	<0.01	0.098	<0.01	<0.1	<0.05	3.01
C	0.011	<0.005	<0.01	<0.1	<0.05	0.435

the whole model, the efficiency was even higher: Experiment A 99.6 %, B 99.5 % and C 99.5 % (Figure 2). Nearly all Cu was retained already in the first compartment of the model. High efficiency in Zn removal was achieved already after the flow through the first compartment filled with sand (97.6 %) and with the mixture of peat and sand (99.4 %) (Figure 2).

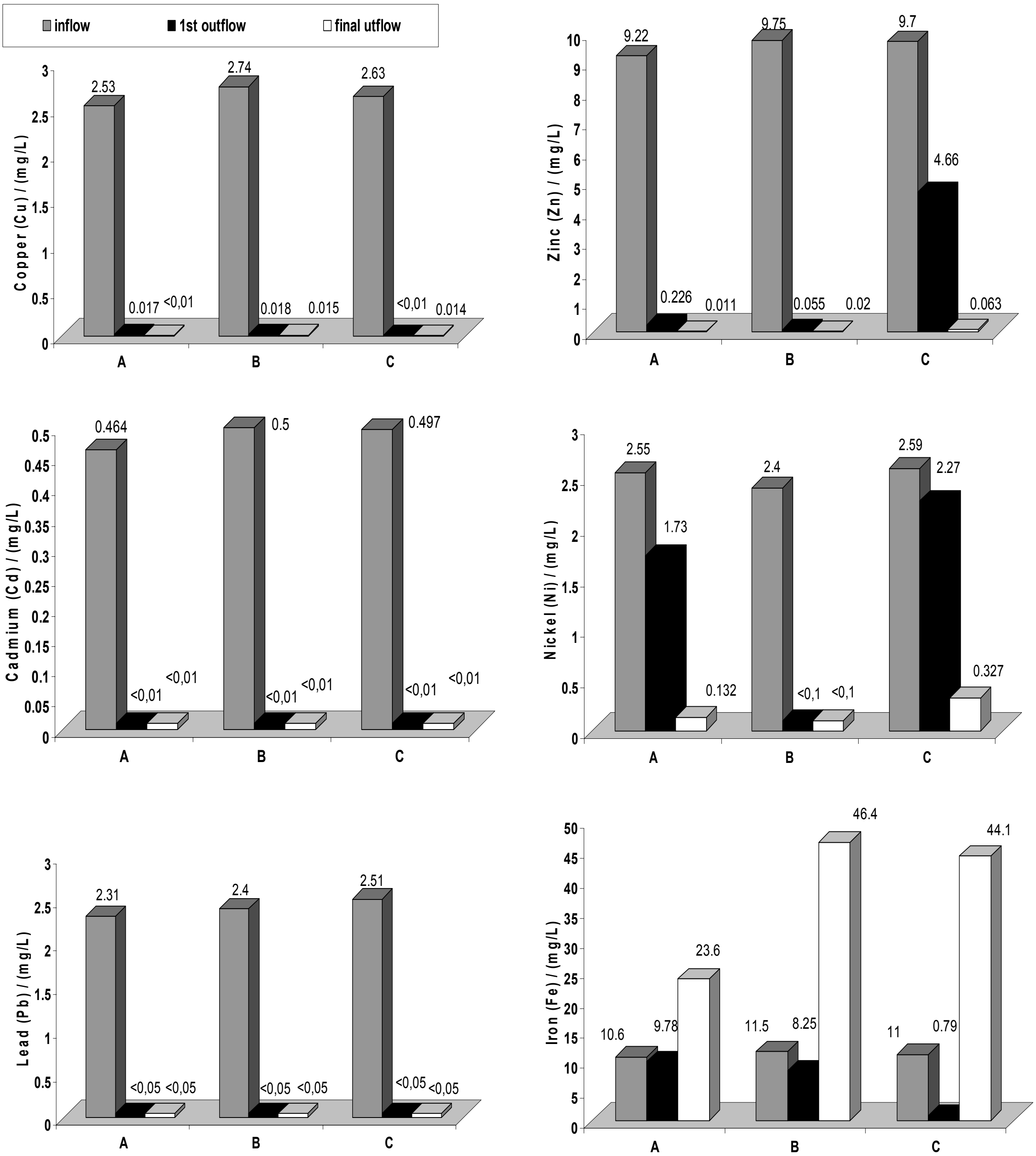

Figure 2.

Metal concentrations in the prepared wastewater at the beginning of the experiment (inflow) and after five days of water percolation through the first compartment (1st outflow) and through the whole model (final outflow) in three experiments: A (sand/sand/sand), B (peat-sand/sand/sand), C (ceramics/sand/sand).

Lower efficiency of Zn removal was achieved with the use of ceramics (52.0 %). In the whole model, the efficiency of Zn removal was high: Experiment A 99.9 %, B 99.8 % and C 99.4 %. The efficiency of Cd reduction in the first compartment was always high regardless of the used substrate (sand 97.8 %, peat-sand mixture 98.0 % and ceramics 98.0 %) and it remained high at the final outflow from the model: Experiment A 97.6 %, B 98.0 %, C 98.0 %. The concentrations in all measured samples were always <0.01 mg/L. Similar low outflow concentrations in all measured samples were found for Pb (<0.05 mg/L). The efficiency of Pb reduction after the flow of the artificial wastewater through the first compartment was high regardless of the used substrate (sand 97.8 %, peat-sand mixture 97.9 % and ceramics 98.0 %) and it was identical to the efficiency achieved in the whole model: Experiment A 97.8 %, B 97.9 %, and C 98.0 %. Therefore, all Pb was retained already in the first compartment. High removal efficiency of Pb was expected as it is an element primarily associated with suspended solids in wastewater, which are expected to be satisfactorily removed during pre-treatment stage of CW treatment (settling). Low efficiency of Ni reduction in the first compartment was achieved with the use of sand (32.1 %) and ceramics (12.4 %). With the use of peat-sand mixture the efficiency reached 95.8 %. High Ni removal efficiency obtained through the use of peat as a substrate was reported by Eger [3]. The removal of Ni was efficient in the whole model: Experiment A 94.8 %, B 95.8 % and C 87.4 %. The inflow Fe concentration of artificial wastewater ranged between 11.5 and 10.6 mg/L. With the percolation of artificial wastewater through the first compartment, efficient removal of Fe was achieved just by the use of ceramics substrate (92.8 %) (Figure 2). The use of sand and peat-sand mixture showed lower efficiency in Fe removal, 7.7 % and 28.3 % respectively. Leaching of Fe was detected in the whole model. The concentrations of Fe were even higher at the outflow from the model than at the inflow of prepared artificial wastewater. It was evident that sand substrate represented a source of Fe, from which Fe leached out in anoxic conditions of the compartments.

The concentrations of Fe were even higher at the outflow from the model than at the inflow of prepared artificial wastewater. It was evident that sand substrate represented a source of Fe, from which Fe leached out in anoxic conditions of the compartments.

The chemical behaviour and solubility of Fe is strongly dependent upon dissolved oxygen concentrations that exist within the water column and substrate layer. Anoxic (reduced) waters and substrates would likely be dominated by Fe^{2+} (soluble ferrous hydroxides – $Fe(OH)_2$) rather than by $Fe(OH)_3$, insoluble solid phase present in oxygenated environment [21]. Considerable part of Fe increase at the outflow can be attributed also to the interactions with other metals present in the artificial wastewater, where exchange of Fe occurred with other metal cations in the solution. The initial concentration of Fe in sewage was also relatively high compared to other metal concentrations (Table 1), as well as inflow concentrations of Fe in the artificial wastewater.

The used mixtures of substrates in the model expressed the capacity of efficient metal reduction from wastewater with the exception of Fe. The majority of metal ions were eliminated already in the first compartment of the model (Table 3). In the compartment filled with sand, the efficiency of metal removal was as follows: Cu (99.3 %) > Cd=Pb (97.8 %) > Zn (97.0 %) > Ni (32.2 %) > Fe, where Fe leached out of the

Table 3.

Efficiency (%) of metal reduction after the artificial wastewater flow through the first compartment of the model in three successive experiments with sand, peat-sand and ceramics used as a substrate.

Experiment	Sand	Peat / Sand	Ceramics
Copper (Cu)	99.3	99.3	99.6
Zinc (Zn)	97.0	99.8	52.0
Cadmium (Cd)	97.8	98.0	98.0
Nickel (Ni)	32.2	95.8	12.4
Lead (Pb)	97.8	97.9	98.0
Iron (Fe)	-	28.3	92.8

substrate. In the compartment filled with the mixture of peat and sand, the efficiency of metal removal was: Zn (99.8 %) > Cu (99.3 %) > Cd (98.0 %) > Pb (97.9 %) > Ni (95.8 %) > Fe (28.3 %). In the compartment with ceramics particles, the efficiency of metal removal was: Cu (99.6 %) > Pb (98.0 %) > Cd (98.0 %) > Fe (92.8 %) > Zn (52.0 %) > Ni (12.4 %). Generally, the lowest reduction efficiency of the selected substrates was achieved for the Ni ion. Ho et al. (22) achieved efficient Ni reduction using Sphagnum peat. High Ni removal (90 %) with the loading rate of 2 mg/L was reported by Eger (3) with ion exchange on peat medium. Crites et al. [2] also reported difficulties in Ni removal in CW with open water surface and good efficiency for Cu, Pb and Zn reduction. Zn and Ni are among others the most mobile heavy metals in soil and ground water [23]. Furthermore, a mixture of metal ions was used in our experiments and their interactions affect their adsorption and precipitation capacity. Tests on bacterial exopolisacharide for the evaluation of the uptake capacity of Pb, Cd and Zn showed that competition exists for the same binding sites between Zn and Cd [24]. Further, in the case of peat, two mechanisms of Pb and Zn cations capture were found out. Pb was specifically bounding on active sites of peat surface, while Zn was subjected to unspecific adsorption.

Based on different sorts of substrate and their physical and chemical characteristics, the mechanism of reduction was different among substrates.

Metal ions in prepared artificial wastewater used in our experiment were present as cations when entering the substrate pore water. Several reactions can take place immediately after the addition of artificial wastewater to the substrate. Metal may complex with other inorganic or organic ions in substrate pore water and thus reduce the concentration of soluble metal ions [25]. Simultaneously, solution metal concentrations may decrease through adsorption or precipitation processes. Adsorption processes are due to an electrostatic bond between the metal and the charged surfaces in substrate. Substrate surface charge is highly depended on pH, with greater negative charge at higher pH. Thus, cationic metals are sorbet most strongly at high pH [25]. Metal cations are removed from solution by precipitation reactions which form new solid phases, usually in association with a corresponding anion already present in the solution [25].

In our experiments, all three sorts of reactions of metal concentration reduction were present. Based on different sorts of substrate and their physical and chemical characteristics, the mechanism of reduction was different among substrates. The major part of complex formation and adsorption processes probably took part in peat substrate with the highest portion of charged surfaces. Peat was followed by sand substrate with higher pore water volume as at the ceramics particles. The crumbled ceramics particles were bigger in size (1 mm – 8 mm) than in sand substrate (1 mm – 4 mm), which most likely caused higher hydraulic conductivity in the compartment filled with ceramics. Shorter retention time together with lower pore water volume in the experiment with ceramics result in low Zn and Ni removal efficiency. Adsorption reactions exhibit time-depended reaction rates [25]. The longer the metal is in contact with soil, the greater is the strength of the bond formed. This increasing strength of bond may be due to diffusion of metal into micro pores on the substrate surface, and there are suggestions that the rate of reaction is metal-specific. Therefore, the rates are as follows: Cd<Mo<Zn<Ni [25,26]. The same order of precedence (Cd<Zn<Ni) in metal removal efficiency was noticed in our experiments using sand and ceramics.

CONCLUSION

As regards the tested substrates, we can conclude that the peat-sand mixture expressed the highest efficiency of metal removal. It was followed by sand and ceramics, which expressed lower capacity in Ni and Zn removal. In this experiment, waste ceramics particles were used, which pointed to the possibility of efficient application of different waste materials in removal of metal ions from wastewater. Similar results with nearly complete metal retention in the first parts of CW were found also by Obarska-Pempkowiak [27], Vymaza and Krasa [28] and Cheng et. al. [29].

The present study provides evidence that tested treatment system can be used efficiently in removal of metal ions already in the stage without addition of plants. Nearly all metal ions were retained in the first compartment of the model, thus metal depositions may be removed by exchanging the substrate in the first smaller beds of CW as these processes are limited by the amount of available exchange sites in the substrate and by the transport of contaminants to these sites.

The results of Fe leaching from the sand substrate directed us towards the need of preliminary testing the substrates meant for the use in CW to avoid leaching in case of its high concentrations in wastewater. Fe is for example a common constituent of municipal landfill leachate or mine drainage, which, when exposed to oxygenated aquatic environments, settles out of the water column to form a thick flock on the underlying layer. This can cause substrate clogging, has a negative influence on microbial activity and results in reduced treatment efficiency of the wetland system. For example, pre-treatment system in the form of easily exchangeable substrate-beds or sedimentation ponds could be incorporated into site designs as a means of minimizing iron levels before wastewater is discharged to a CW.

The longer the metal is in contact with soil, the greater is the strength of the bond formed. This increasing strength of bond may be due to diffusion of metal into micro pores on the substrate surface, and there are suggestions that the rate of reaction is metal-specific.

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Original scientific paper

Personal hygiene awareness among food handlers

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ABSTRACT:
In the globalization and rapid industrial development times food safety assurance is one of the basic conditions for protection of public health. For this purpose knowledge and awareness of personal hygiene among food handlers were determined in one of the middle-sized meat processing plants. It was found out that food handlers are aware of personal hygiene, but do not always practice it. Were observed problems in inter – social relations and communication difficulties at all levels, which can influence on quality of work performed and consequently on food safety assurance. Awareness of importance of good hygiene practice is based upon sense and is not uniformed. Periodicall, thematicall and methodologicall adapted trainings are crucial for food safety.

KEY WORDS:
Food safety, Personal hygiene, Employees, Food industry

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INTRODUCTION

Food is basic human good and need. So in this period of globalization it is very important to control food safety from "stable to table" and in accordance with legislation. From January 1st, 2006 legislation is harmonized in all European Union (EU) member states [1,2]. An obligatory tool for food safety assurance, so-called HACCP system, enables food operators to identify hazards at individual stages of technological process and to control those hazards by continuing and systematic control. The HACCP system must be based upon solid grounds – pre-requisite programs (PP). PP include hygiene programs and activities, necessary for involvement and execution of the HACCP system as an internal control in food businesses [2].

HACCP system is very structure and easy to manage, because requirements as written down in forms of strategies. It can be adjusted by every company with regard to the type and size of food business. But authors of professional and scientific papers are questioning regarding its efficiency in practical work [3,4,5,6], mainly in large and small food businesses. Important elements of HACCP systems are job satisfaction and motivation [7,8], which in food businesses are often ignored or put away. Successful companies have experienced that the biggest challenge nowadays is not developing corporate vision and defining strategies, but establishing a system, which stimulates employees to follow it [9]. Experiences in the field of human resources management have shown employees must be dealt with as whole persons. So the management must stimulate employees to work effectively. One of the ways is to motivate the employees by organizing work at operative levels [10].

Hygiene principles and responsibilities

Food production and trade must be in accordance with principles of good practice. Responsibility for food safety is divided between food operators and each and every employee, which must performs duties according to rules.

Food operators must assure food safety in all the stages of production and trade by implemented internal HACCP-based control. Documents and records of all the stages of preparation, planning, implementation, activities, control and eventual HACCP system changes must be kept. Employees must be supervised, must be instructed, and their continuous training regarding hygiene of foodstuffs must be taken care of, according to significance of their work. For this purpose a yearly plan of specific and continuous training, which is a part of PP documentation, must be elaborated. Only persons with suitable food education or professionally trained person are allowed to work in food production and trade. At the same time they must follow the rules of good practices [2], relating to personal hygiene, health status, protective clothing, suitable footwear and prohibition (e.g. chewing, smoking, eating etc.).

Food operators must assure food safety in all the stages of production and trade by implemented internal HACCP-based control.

The aim of the research in the selected food business was to have a total insight into employees' knowledge and awareness regarding personal hygiene while handling food.

METHODS

In the research a combination of quantitative and qualitative methods was used. The latter enables complete and deep studying, namely from both statistical and text analysis aspects. If the combination of the mentioned method is sensible was and still is a subject of many discussions in Slovenia [11]. Use of qualitative methodology enables a deep insight in experiencing and comprehension of the studied phenomenon and involves personal experiences. By the combination of quantitative and qualitative methods[1] it was determined how personal hygiene is experienced and comprehended by interviewed employees. Their everyday work was observed as well.

[1] The methodology and the results, which are presented in the paper, are the part of the graduation research by Špela Hajdinjak. The graduation research was carried out in Department of Department of Sanitary Engineering of College of Health Studies in Ljubljana.

Quantitative method

In the quantitative part of the research employees' knowledge of the HACCP system, pre-requisite programs, food safety assurance and general feeling in a company were determined by a questionnaire [12]. The questionnaire was fulfilled by 84 out of 117 production workers. The respondents fulfilled the questionnaires with presence of a researcher. It took place from July 7th till August 8th, 2006.

The research was very extensive, so in this paper only the results regarding employees' knowledge of principles of good hygiene practice in the selected food business are presented.

By the combination of quantitative and qualitative methods it was determined how personal hygiene is experienced and comprehended by interviewed employees.

Quantitative method

To gain deep insight into the discussed problems a method of structured interview and a method of observation of work practices were used. By using partly structured interviews opinions of ten workers and three food experts regarding importance of personal hygiene during food handling were determined. The importance was attached to hand-washing, understanding of the term "safe food" and trust in food safety "from stable to table". The interviews in the selected company took place on August 3rd and 4th, 2006. The results of comprehension of the terms regarding food safety and hand-washing are presented in the paper.

Observation of work practices took place from July 7th till August 8th, 2006. During observation of a working process we focused on protection during food handling, behavior of food handlers and following of good hygiene and production practices.

RESULTS

The questionnaire

Four questions were included in the questionnaire. The questions were related to the knowledge of principles of good hygiene practice with main stress laid upon personal hygiene during food handling.

Most of the workers use preventive when and where necessary (table 1). But quite few of them do not cover infected wounds (23.8%) or pimple (20.2%).

Table 1.
Use of protective clothing during food handling.

During food handling I cover...	n	Yes /%	No /%
… mustache, beard and long hair with a hair net.	83	96.4	2.4
… plaster placed over a wound with gloves.	82	94.0	3.6
… nail polish – with gloves.	79	75.0	19.0
… a short hair – with a head covering.	82	94.0	2.4
… a pimple – with a plaster.	80	75.0	20.2
… hand jewelry - with gloves.	80	77.4	17.9
… infected wounds – with a plaster or a bandage.	82	72.6	23.8

A gender of the respondents significantly ($p<0,05$) influences the statements "During food handling I cover nail polish with gloves", "hand jewelry with gloves", "infected wounds with a plaster or gloves". A difference between the respondents, who cover nail polish and hand jewelry and those, who doesn't is higher among men than in among women. Women covered infected wounds with a plaster in a higher degree compared with men.

The majority of the employees answered that in cases of diarrhea, vomiting, fever etc. they do not handle food (table 2).

Table 2.
Health status of employees and employee involvement in the working process.

I handle food, when I ...	n	Yes /%	No /%
… have diarrhea.	84	1.2	98.8
… feel dizzy.	84	20.2	79.8
… have a cold.	84	3.6	96.4
… am exhausted.	83	33.3	65.5
… cough.	83	8.3	90.5
… have a high body temperature.	84	9.5	90.5
… vomit.	84	0.0	100.0
… cut myself.	84	13.1	86.9

24 different combinations of answers were determined by the analysis of the answers to a question: "What do you think are the three types of inconsideration of hygiene principles, which directly influence food safety?". The respondents could choose among ten possible activities. The results are shown in table 3.

The respondents chose this combination of answers (1) "I don't wear head-covering" most frequently (29.5%), (3) "I wash my hands after using the toilet" and (6) "I use dirty working utensils". All the answer, which could not be ranged into none of the most frequent combinations of answers and were answered infrequently were joined in a group "other".

Table 3.
Hygiene principles, which directly influence food safety.

Combinations of answers	%
1, 3, 6	29.5
3, 5, 6	14.1
3, 4, 6	8.9
1, 2, 3	7.7
3, 5, 10	5.1
Other	34.7

Legend: 1 – "I don't wear head-covering", 2 – "I wear jewelry during food handling", 3 – "I wash my hands after using the toilet", 4 – "I don't have clean overall", 5 – "I forget to clean my work place", 6 – "I use dirty working utensils", 7 – "I chew while working", 8 – "I wear nail polish", 9 – "My protective footwear is dirty", 10 – "I've forgotten to clean a refrigerator".

The employees' knowledge of HACCP system and pre-requisite programs was determined by a question regarding factors, which are, according to employees' opinion, the least important for food safety (table 4). The results show that employees think personal hygiene is one of the most important factors for food safety, because only 1.2% of them believe that personal hygiene do not influence food safety.

Table 4.
Factors, which according to workers influence food safety.

For food safety I think it is important to…	%
… measure a food temperature.	2.4
… check the date of durability.	4.8
… check food quality.	27.4
… follow personal hygiene principles.	1.2
… assure suitable working conditions.	17.9
… check a concentration of a cleanser.	19.0
… measure an air temperature in cold warehouses.	3.6
… record measured and read parameters.	20.2

According to respondents' opinion quality control of foodstuffs (27.4%), control of cleanser concentrations (19.0%) and suitable working conditions (17.9%) are less important for food safety. Employees don't see the importance of recording measured or read parameters (29.2%)

The partly structured interview

Connections between laic and technical definition of the term "safe food" were assessed by the content analysis of the respondents' answers. The statements with similar contents were joined into categories, which were named as associations. The definition written in the Act Regulating the Sanitary Suitability of Foodstuff, Products and Materials Coming into Contact with Foodstuffs was used as a base for a technical definition of the term "food safety". In the Act food safety is defined as follows: "food safety is assurance that foodstuff is not harmful for human health, if prepared or used for its intended purpose [13]. As an acceptable answers were considered statements like e.g. "sage for consumer", "healthy" or "not harmful". All the other answers were determined as incorrect. It was found out that only one respondent explained the term “safe food” complexly and came near to the technical definition of the term. The results evidently show the majority of the respondents relate the term safe food to a health hazard (61.5%). The rest of them connect safe food with health (15.4%) and a working process (15.4% (table 5). Only one respondent mentioned control as well.

Table 5.
Content analysis of answers employees had, when asked to define the term “food safety”.

Mark	Association	n (%)
A	Hazard	8 (61.5)
B	Health	2 (15.4)
C	Working process	2 (15.4)
D	Control	1 (7.7)

The next question to the employees was what was their first thought when they heard the expression “wearing of overalls is obligatory” and what is their relation to it. The resul ts showed that all of the employees are aware of the importance of wearing overalls, because they believe wearing overalls is necessary and obligatory. The respondents’ opinion is that the main purpose of wearing overalls is personal protection and that food protection is secondary.

Opinions regarding hand-washing were determined afterwards. The respondents were first questioned what they thought of when they heard the term “hand-washing”. Most of the respondents they think of hygiene and quality (30.8%). Two respondents connected hand-washing with protection or protection and hygiene (table 6).

Table 6.
Analysis of what were employees’ first thoughts, when they heard an expression “hand washing”.

Mark	Association	n (%)
A	Hygiene	7 (53.8)
B	Quality	4 (30.8)
C	Protection	1 (7.7)
A+B	Protection and quality	1 (7.7)

Observing

For the results of observation it is necessary to stress out that deficiencies were determined for individual persons and the results can not be concluded for all the employees in general.

Protective clothing

- All production workers used protective clothing and equipment required for production process.
- Women did not use disposable head-coverings properly, because hair is not completely restrained.
- In the past men wore caps made of cloth (baseball caps). Some of the workers still keep the caps in their lockers, although it is not allowed. Some of them still use the caps instead disposable head-coverings.

- Workers from the micro-confection department did not dispose face mask and gloves in the marked waste basket when leaving the room.
- Some of them didn't change overalls during work, although they were already dirty.
- During inspection of area and equipment in the cutting department a worker from micro-infection was momentary present. There was a possibility of cross-contamination because workers could move from high to low risk areas and back and forgot to change their clothes at the same time. They forgot the hygiene barrier is essential.

Hand-washing

- During our observation there was nobody passing by hygiene barrier. Two workers were randomly selected and wet swabs for hand hygiene were taken from their hands. Results of microbiological analysis did not show presence of pathogenic bacteria.
- Workers wash and disinfect their hands at hygiene barrier located at the entrance, but didn't do the same when entering the production area, although they should.
- When drivers entered the dispatch area, they didn't use the hygiene barrier located at the entrance, although the latter are located at every entrance. They didn't use disposable head-coverings as well.

Observation of the working processed showed that irregularities in hair coverings are even more frequent as showed by the results of interviews.

Other hygiene and/or irregularities

- During veterinary inspection a worker had to leave his work place, because his beard was not properly tidy.
- On of the female workers wore too much make-up, although a supervisor warned her.
- Workers, who wore ring during work didn't use disposable gloves.
- Some of the production workers do not follow ban rules (e.g. chewing, eating).

DISCUSSION

The results of interviews and observation of working process show a slightly inconsistent following of GHP principles and employees' awareness of the latter. The interview analysis showed that 2.4% of respondents do not cover mustaches, beard or long hair with a hair net and that 2.4% food handlers do not cover short hair with a head-covering. Observation of the working processed showed that irregularities in hair coverings are even more frequent as showed by the results of interviews. Hair may be contaminated with numerous micro-organisms and dirt (e.g. dust, dandruff), which can be transmitted on foodstuffs, so principle of not touching is very important [14]. Some of the workers wear jewelry while handling food and do not use disposable gloves. Some of them use disposable gloves, but do not change them according to principles of good hygiene practice. Microorganisms under jewelry worn by workers can not be washed away during hand-washing, which increases a possibility of food contamination [14]. A negative thinking of good hygiene practice among workers was not noticed. Similar findings are stated by some other authors, too [15,16]. A negative thinking of the HACCP system was clearly presented in a qualitative study, which included an owner of a small farm in Great Britain. He thought that HACCP system is a "bureaucratic nightmare" and that recording of performed activities does not influence food safety [4], which was also the case in almost the third of answers of the respondents in the presented research.

During observation of the working process bad mutual relationships and communication problems between workers and some of the supervisors were seen. Too authoritative attitude towards all the employees was noticed, as well. The mentioned troubles result in inferior feelings among employees, which de-motivate them. This can significantly influence work aiming food safety. The mentioned fields of human resource management and management techniques should be adopted by management and experts in food businesses through training.

CONCLUSION

Food safety is a responsibility of both the management and the food handlers. Therefore their knowledge, awareness and behavior are crucial for food safety assurance. Beside improperly planned trainings about good hygiene practice and good production practice, bad mutual relationships, communication problems, authoritative attitude and lack of motivational approaches are the reasons for unsuitable behavior of employees. The majority of the respondents show a positive attitude towards the HACCP system and good practices, which is also reflected in their work, but there are still some individuals, who do not follow rules. By observing the working process it was determined that employees are aware of their faults, but nevertheless repeat them. So awareness of the problems remains at level of reasonable comprehension, but it is still not incorporated into practical work. Food safety management is not limited to identifying and estimation of hazards, but includes their control as well. The responsible persons have an important task to establish an effective communication among co-workers both vertically and horizontally, to prepare effective and specific trainings for employees and to find ways for motivating both individuals and groups. To improve hygiene in a company a positive attitude of all employees is important. Motivation is important as well, because it influences workers attitude towards their work, their superiors and towards a company.

HACCP system is a strategy of food safety assurance and requires adjustment of a process regarding size and volume of a food business. A comprehension of system's and legislative requirements by the responsible persons, who are often unmotivated or have insufficient knowledge regarding food safety, is important. A total food safety management should be oriented to constant improvement, which would influence training of employees and managing system requirements and employees' attitude towards work.

HACCP system is a strategy of food safety assurance and requires adjustment of a process regarding size and volume of a food business.

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Original scientific paper

Food safety assurance on tasting field

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ABSTRACT:
Hygiene and technical requirements, which must be met by the tasters and people who organize tasting are clearly presented in this article. A hygiene-technical estimation of the actual situation in tasting is described. Two years of researching in the field of tasting brought the following results: tasting is not included in the regulations and guidelines; tasting are performed by the personnel, who are not suitably educated regarding food safety; enterprises, which organize tasting do not educate their tasters regarding food safety; there is no control over enterprises and their tasting performers. The presented results will be used as a basic for preparing of a model of correct tasting performance with consideration of hygiene, technical, technological, and health criteria. From the food safety point of view the field of tasting is not managed as it should be, therefore the health of people, who participate in tasting, is threatened.

KEY WORDS:
Tasting, Education, Hygiene, HACCP system, Legislation

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INTRODUCTION

The term "tasting" defines supply of food, which must be suitable for consumers, therefore food preparation must meet the minimal hygiene criteria, regardless of location of food preparation [1].

Two years of experience with tasting organization showed lot of deficiencies in surveillance of this filed and hygiene-technical deficiencies in tasting performing. Nowadays everybody is allowed to perform tasting, regardless of previous knowledge. Tastings are organized by various companies, which do not enable additional training regarding food hygiene and good hygiene practice to tasting performers. Many of food producing companies decide, due to economic reasons, to perform training by themselves. Tastings are mostly thought as a commercial events, because first of all companies are interested in sale success during tastings. Hygienic food preparation and food offer are put in the rear and are not important to the customers of tasting performers [1]. For food safety assurance it is important to define, control and manage each and every link in the food/supply chain. There is a simple rule that food is and will be safe if each person included in the "from stable to table" food chain understands and performs its duties and tasks [2].

The basic hygiene-technical principles are regulated by law, which is harmonized with EU law.

On the one hand enormous increase in food chain volume in the past decades and on the other hand various trouble-causing and new micro-organisms caused the need of system, which is able to assure global food safety. This was reason for forming of HACCP system, which is based upon an effective internal control [3]. The system was originally developed as a system for microbial safety to provide safe food for space expeditions. In 1971 the system was presented at first American National Conference for Food Protection. In 1993 the HACCP system was included in the European food legislation [4,5] and from January 1st, 2006 the HACCP system is obligatory for all EU non-primary food operators [6,7]. In Slovenia the system is obligatory for all players in food production and trade from January 1st, 2003 onwards [8].

Food safety assurance must be discussed as a whole and requires active cooperation among all links of food/supply chain. The basic hygiene-technical principles are regulated by law, which is harmonized with EU law. Food safety is responsibility of food operators.

To assure safe food for consumers, pre-requisite programs and procedures must be based upon HACCP principles.

Tasting law is lax, so requirements are interpreted by each taster on his own way. For foods placed on the market general hygiene-technical requirements are defined, but tastings are not included in the term "foods on the market" directly. The following is required in preparing and execution of the tasting event, which is undoubtedly part of "foods on the market":

- Educated and trained tasters;
- Suitable hygiene-technical place for execution of the tasting event;
- Suitable waste management;
- Following food hygiene principles and HACCP system.

HYGIENE STANDARDS FOR EXECUTION OF THE TASTING EVENT

Receiving foodstuffs

Tasters must check safety criteria and foodstuffs quality at receiving (e.g. date of durability, packaging integrity, and temperature). From January 1st, 2006 onwards introduction of HACCP system is obligatory for all included in food production and trade (during storage, transport and handling food is, with the exception of primary one, exposed to biological, chemical and physical hazards). Inappropriate food handling, mainly broken cold/warm chain, unconsidered dates of durability and un-separated high/low risk procedures/areas enable survival and multiplication of bacteria, even toxins formation. Inappropriate food handling can be the cause for food poisoning. To avoid the latter employees must follow food hygiene principles. Practices and procedures which ensure good hygiene practice must be based upon the following principles:

- Avoid or limit contamination (pollution) with undesirable microorganisms,
- Avoid or limit multiplication of undesirable microorganisms,
- Avoid the undesirable multiplication of microorganisms,
- Avoid the intolerable survival of microorganisms or their metabolites.

Inappropriate food handling, mainly broken cold/warm chain, unconsidered dates of durability and un-separated high/low risk procedures/areas enable survival and multiplication of bacteria, even toxins formation.

Before starting the tasting

Tasters must be healthy and qualified for food handling.

Health status of a taster

Taster with infected skin wounds, sore throat, diarrhea, increased body temperature and if he/she vomits, he/she is not allowed to handle food. Tasters must notify the food operator of his/her superior [7].

Harmful bacteria are transmitted in foodstuff from a sick person or from an infected person who is capable of transmitting bacteria, before he/she is taken ill. Such a transmission can be prevented by good hygiene practice, especially by proper hand hygiene. Large amounts of bacteria and virus, which cause food borne infections, are secreted in feces of sick persons and some of them in urine. Microbes are secreted in person's fluid droplets through the nose or through the mouth. Up to 10^9 of salmonella cells per gram of feces are secreted in feces of salmonella carriers in convalescent-stage [9]. Infected skin wounds are the source staphylococci and streptococci. Enterotoxic staphylococci are bacteria, which cause food borne intoxications. During favorable conditions in a foodstuff staphylococci are rapidly multiplied, some of the strains even form toxins [10].

Personal hygiene for a taster

Food handlers must practice a high level of personal hygiene and must wear clean and suitable overalls [7]. Food handlers must keep fingernails short and must not wear nail polish. Hair must be covered or kept tied back if it's long. Food handlers must not wear jewelry or hand watches. Protective overalls must be worn. Before work hands must be washed properly to wash away dirt and existing microflora. Hand hygiene must be kept during work to avoid cross-contamination and by that contamination of foodstuffs. Hands must be washed after visiting the toilet or after every high-risk procedure. Proper hand washing removes the dirt and microorganisms from skin. The technique: wet your hands with warm water, apply soap and rub your hands together for at least 15 seconds [9].

Food handlers must not touch ready-to-eat foods with their bare hands, but must use clean utensils. In some cases (e.g. sausage cutting, high-risk foodstuffs…) as a preventative measure food handlers must use disposable gloves for performing individual tasks. When gloves get dirty or damaged ensure that they are changed, because microorganisms can penetrate through. Skin gets wet during work and permeability of gloves materials increases [9].

Preparing the work place

When handling food the hygiene-technical requirements for food preparing, processing, finishing and selling areas must be met. To avoid cross-contamination of foodstuffs the sinks with cold and hot running and drinking water must be provided [7].

Food heat treatment must assure microbiological safety of food and must preserve all food nutritional and natural goodness.

Utensils (e.g. tableware, cups, boars, plates), which are used during tastings must be stored on a clean work surface. Cups should be stored upside down on a clean serviette to avoid contamination of cups (e.g. by talking). When Spoons and forks are placed down, the handles should be lifted to reduce chances of cross-contamination. Scoops, ladles, whisks should be placed on a clean surface (e.g. a clean plate). The pallets and shelves with goods should be lifted off the ground.

Assuring regimes for temperature

Microbiologically perishable foodstuffs need to be stored at temperatures, which do not assure the right conditions for harmful micro-organisms growth or toxins formation, which are hazardous to health. As a rule cold/warm chain must not be broken, only short periods of decline in temperature are exceptions, when temperature is controlled due to special food handling during preparing, transport, storage, selling and serving. Theses periods must be as short as possible [7].

During tastings attention should be paid to foodstuffs, which requires handling at a certain temperature. Every time taster must supplement missing foodstuffs, because larger provisions would represent a potential hazard for microorganisms development (e.g. *Yersinia enterocolitica, Listeria monocytogenes*, some strains of *Clostridium botulinum* grow slowly at temperatures around 3°C) [9]. Because of people in the immediate vicinity food contamination must be prevented during tasting. Perishable foodstuffs must be handled at temperatures below 5°C [11].

Food heat treatment must assure microbiological safety of food and must preserve all food nutritional and natural goodness.

For food safety the core temperature must kill non-spore-forming harmful microorganisms (at least 74°C) [11]. To assure that a temperature and time of heat treatment must be monitored. Re-heating of cooked food must be quick, to pass over temperature interval between 10 in 60°C as soon as possible. Re-heated food must be served at once and at temperature of at least 63°C. In such a manner food will be safe and will preserve its organoleptical properties [9].

Literature review and experiences showed tastings are not suitably controlled from the health point of view and is not suitably dealt with both in expert circles as in science circles. The latter was the reason for research, which aimed to determine current methods of tasting control and tasters' knowledge about basic hygiene principles and HACCP system.

METHODS

A combination of quantitative and qualitative methodologies was used in the research. For the quantitative part of the research a questionnaire was prepared, which was composed of two parts. In the first part data about tasters' training and execution of tasting events were obtained. In the second part tasters' knowledge about good hygiene practice, cold/warm chain and knowledge about the current food hygiene legislation were checked.

The questionnaires were distributed among randomly selected tasters, who were present in the shopping centers IS-BTC in IS Vič during interviews. Tasters were divided in two groups: the first group was "pkk" group of tasters, who have the expert guidance and the second group was "ad hoc" group of tasters (mainly handling poultry products) with non-professional and non-expert approach – tasters were left to their own resources. They were interviewed during weekends, from May until early August 2005.

Tastings were also executed in areas, which did not meet the minimal hygiene-technical requirements.

In the qualitative part we used a method of observing for evaluation of execution of tasting events and following the food hygiene principles during tastings.

RESULTS

20 tasters from pkk company, which professionally organize tastings (the group A) and 20 tasters, which were hired by food producers (the "ad hoc" group) of various brands (mainly poultry products) (the group B) were interviewed.

Analysis of execution of tasting events

We determined that tasters are not supervised, so taster can be anybody, who is hired by a company irrespective of as to whether the hygiene requirements are met. We did not find any records about official inspections. Tastings were also executed in areas, which did not meet the minimal hygiene-technical requirements. Requirements for temperatures of both hot and cold food holding were not met. During tastings and transport temperatures were not controlled. Food was transported mainly in personal cars, which are not equipped for food transport.

People working in companies, which organize tasting events are not suitably educated about foodstuffs, which is reflected in tasters themselves. As a rule the minimal hygiene-technical conditions are not assured (e.g. suitable hand-washing sink).

Tableware and dishes intended for consumers are usually disposable. Waste is not separated (according to origin) and is disposed near tasting tables. We did not see any records regarding tasting management.

Tasters' knowledge and qualification

Twenty tasters from the group A and twenty tasters from the group B were interviewed. Manly girls were employed as tasters; 18 of them in the group A and 11 girls in the group B. tasters were from 18 to 50 years old. The age of the majority of the tasters was between 18 and 25.

Table 1 shows that companies hire persons, who do not have any certificates of training. 16 tasters out of 20 hired by pkk company posses a training certificate, while in the group B only 7 persons out of 20 were trained. The majority of tasters are not familiar with legislative requirements for tastings, because they believe they should repeat the training every 5 years. Tasters hired by pkk company are educated regularly and are prior tasting event always informed about properties of products, which are tasted. The opposite was found out in the group B. they weed instructed regarding hygiene of foodstuffs manly during various courses, which were organized by competent institutions (e.g. The Institutes of Public Health); some of them gained knowledge during their schooling. Education was organized by employing company for none of the group. It was determined that the majority of tasters form the group B posses no suitable certificates (e.g. conformity for obligatory illness report, certificate of training regarding hygiene of foodstuffs) before starting to execute a tasting event. Only 15 tasters from the group A possessed all the certificates, required by the Rules on hygiene of foodstuffs[1] (which was repealed). Most of the tasters are not familiar with the significance of uninterrupted food cold chain, because they rather guessed than know the temperature assuring food safety. The proper temperature was stated by 11 tasters from the group A and 7 tasters from the group (Table 1).

For heat treatment of food heaters, cookers and ovens are used. For food safety it is important to keep food warm at temperatures above 63°C. It was determined that the majority of the tasters are not familiar

[1] Rules on hygiene of foodstuffs (Official Gazette of RS, No. 60/2002, 104/2003, 11/2004, 51/2004, 54/2007), Rules-repealing the Rules on hygiene of foodstuffs (Official Gazette of RS, No. 54/2007).

Table 1.
The results of interview, carried out in the both groups of tasters in 2005 [1].

Activities	The group A (n)	The group B (n)
Certificate of food hygiene training	16	7
Information regarding regular yearly training	11	4
Commercial and food hygiene knowledge	19	2
Presence of declaration of health status	15	2
Knowledge about the cold chain	11	7
Knowledge about the warm chain	12	5

with the significance of unbroken warm food chain. 5 tasters from the group B and 12 tasters from the group A answered correctly.

DISCUSSION

Tastings are currently considered only as commercial events, because only selling of promoted products is important. The only pointer of successful tasting is increased sale.

Tasting can be executed by anybody, because there are no legislative restrictions, although food handling is indubitable defined in Regulation on the hygiene of foodstuffs [7].

Specific minimal hygiene-technical requirements on tasting preparing and execution are stated in EU Regulation on the hygiene of foodstuffs [7] as the term “foods on the market”. Figure 1 shows basic topic, which are controlled by food business operators on the one hand and by competent inspections on the other hand.

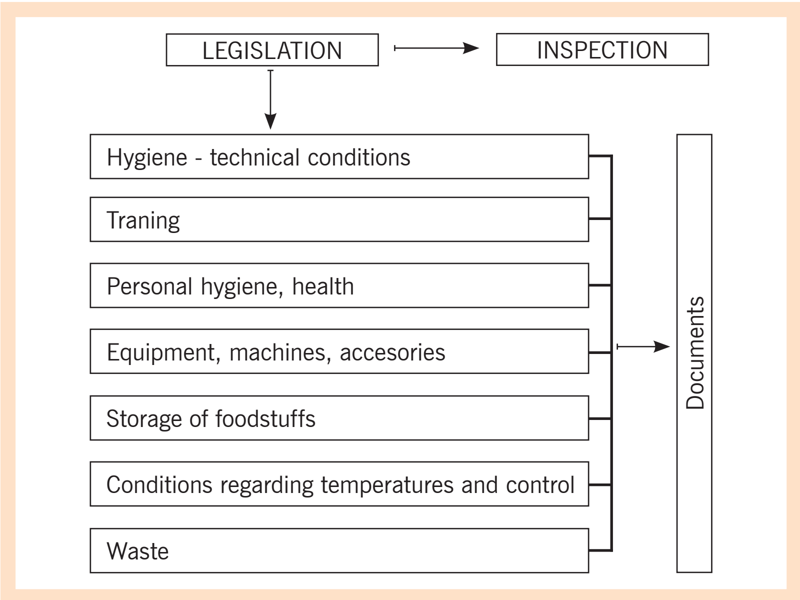

Figure 1.
Minimal requirements for food safety during preparing and tasting.

It was determined that tastings are not sufficiently controlled by competent inspections or they are not controlled at all. Two years of experience with tasting organizing showed some of deficiencies and irregularities both in hygiene-technical and organizational aspects. One of the most frequent irregularities was that tasters are not suitable supervised, which leads to:

- Insufficient knowledge of promoted products (composition, properties, additives…),
- Usage of inappropriate utilities for tastings,
- Inefficient maintenance of warm/cold food chain,
- Inappropriate food and product handling from hygiene point of view,
- Inappropriate tasting waste management.

Preparing and execution of tasting is very complex and requires educated and trained tasters as well as suitable hygiene-technical conditions in places, where tastings are executed. Food handling, according to food type and considering cold/warm food chain are important. Cold/warm chain of perishable foodstuffs must not be broken during transport and in stores. Larger stocks of promoted perishable foodstuffs must be assured for each store In order to assure safety rather than to transport foodstuffs in cars, which are not designed for food transport.

Required temperatures, both high and low ones, for promoted products must be kept. Therefore it is important that refrigerators are located near place, where tastings are executed. If heat treatment of foodstuffs is needed, tasters should check the temperature during heat treatment and should keep food warm. It was determined that temperatures are not measured, so there's a potential hazard for peoples' health.

Educators of tasters can only be professional educated persons. It was determined that tasters are nor sufficiently informed about hygiene of foodstuffs and personal hygiene during food handling.

Tasting waste must be stored in suitable and covered containers. Organic and other waste must be collected separately. Waste baskets must be emptied regularly and after work must be cleaned with water. Taster do not separate waste according to type and waste is collected in open carton baskets, located on the floor and by the tasting desks, which is in opposition to hygiene principles and legislative requirements [7]. Food operator is responsible for food safety assurance during production and trade. Hygiene programs and procedures, which are necessary for internal HACCP system execution in food business must be assures. A responsible person for internal control can be designated by a food operator. Such a person must be educated about food hygiene and HACCP system principles. Food operators must elaborate a yearly plan of training. Food handlers in production and trade must demonstrate the knowledge about hygiene of foodstuffs. Knowledge about hygiene of foodstuffs can be gained by technical education or by additional training regarding food handling [7].

Educators of tasters can only be professional educated persons. It was determined that tasters are nor sufficiently informed about hygiene of foodstuffs and personal hygiene during food handling.

CONCLUSION

It was estimateds that tastings are considered as "foods on the market" as well, so all legislative requirements regarding food safety must be met.

During tastings food preparing and trade are weaved, so collaboration of tasters and clients. A taster must meet all the legislative requirements regarding food safety, while clients must provide suitable place for tastings, meeting all the hygiene-technical requirements. Tasters can be persons with the knowledge about hygiene of foodstuffs and of promoted products. Nowadays consumers are of great pretension and are aware of nutrition and food additives. This is why a taster must know to answer all kinds of questions and dilemmas to consumers. By following the hygiene-technical principles taster can contribute to improve hygiene culture during tastings and can influence hygiene awareness of consumers.

Because tastings are constantly executed mainly in middle-sized or large shopping centers and because there are more and more tasting organizing companies, yearning for profit, the educational materials exclusively written for tasters should be prepared. The existing educational material about hygiene of foodstuffs is not adapted to mentioned topics. The knowledge, which tasters gain during food hygiene courses are not adjusted to specific topics of their work, since their work is completely different as work in a kitchen, where suitable running and drinking water is always available. The existing courses offer general knowledge regarding hygiene of foodstuffs and lot of tasters can not relate those topics to their work.

From the determined state of affairs it is concluded intensified severity of inspection is needed, which could stimulate a transparent demonstration of safe tasting processes. Tastings should by no means threaten health of consumers. Only a qualified taster, with all the technical support and the knowledge of food hygiene, can be an active partner in food/supply chain and trustworthy part of food safety assurance.

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Original scientific paper

The amount of active hydrogen in selected juices and teas on the Slovenian market

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ABSTRACT:
The ageing process is influenced by increased oxidative stress, which causes damage to cellular components, such as DNA, proteins and lipids. Many studies claim that use of antioxidant might prevent intracellular oxidative damage formation and thus decrease the incidence of age related diseases (cancer, cardiovascular diseases, cataract...). The level of endogenous antioxidants cannot be deliberately increased. However, the level of exogenous antioxidants intake can be increased by consuming more fruit, vegetables or their juices, which are a rich source of many different antioxidants. Today consumers are aware of a healthy way of living, thus the antioxidant status of a product can be important information in the decision of purchase.

We measured the antioxidant status in selected fruit juices and teas. Since each exogenous antioxidant (vitamin C, E, beta carotene) prevents oxidation or quenches free radicals by donating one electron or H^-. For this reason the amount of active H (H^-) was determined as an indicator of the total antioxidant potential. Besides, the intake of H^- with natural products is better than with synthetic ones, because fruits and vegetables contain many different antioxidants which can regenerate each other. It was concluded that the total antioxidant potential, measured as the relative amount of H^- (partial H pressure), is a better indicator of the antioxidant status of a specific food product, than the determination of only one specific antioxidant, eg. vitamin C, E or beta carotene. The results indicate significant differences in the rH level among different drinks. The highest value of active hydrogen was determined in tomato juice, red grapes juice, carrot, blackcurrant, nectar of strawberry, apple and grapes, orange juice, pineapple juice, sour cherry nectar and blueberry tea. There is much active hydrogen also in the pear nectar, apricot nectar, peach nectar, banana nectar, nectar made of seven juices and five mashes, but these are with added synthetic antioxidants (ascorbic acid) that contribute to the increased value of active hydrogen. The antioxidant potential of teas is lower than the antioxidant potential of the majority of juices. However, the portion of active hydrogen is in all selected beverages is much larger than in potable water.

KEY WORDS:
Active H, Antioxidants, Oxidative stress, Juices, Teas

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INTRODUCTION

Currently, many researches are being conducted on vitamins mainly in the two fields: in the field of the daily needs and recommended daily intake of vitamins and minerals, and in the field of ageing prevention, oxidative stress, cardiovascular diseases and cancer [1].

Antioxidants are substances that slower or prevent the oxidation of important cellular components in various ways. After the reaction with the radicals antioxidants are transformed into more stable products or less noxious radicals, which are not reactive enough to cause free radical mediated chain reactions. Mostly, after the job is finished, antioxidants are worn-out. Some (ex. vitamin C and vitamin E) renew and regenerate in the oxidation-reduction processes.

Results of basic researches discovered an important role of vitamins in the pathophysiology of diseases connected with oxidative stress [2,3] such as: arteriosclerosis, hypertension, cataract, rheumatic arthritis, malign diseases, Parkinson's and Azheimer's diseases [4-6]. Epidemiological studies determined a lower rate of cancer, heart and veinal diseases between persons that with food consumed higher quantities of vitamins C, E and β-carotene. An increase of the serumal level of these vitamins was noticed in these persons [7-9]. Until now, researches ascertained a lower break out of cancer, heart and veinal diseases only between people that consume enough quantities of fruit and vegetables, but not between people that consume supplements of vitamins [10]. The consumption of fruit and vegetables lowers the formation of free radicals in the body and thus the induced oxidative lesions of the DNA, meanwhile many studies show that only supplements of vitamins C, E and beta carotene do not lower DNA lesions [11-15]. Researches confirm that is best if the protective substances (antioxidants and vitamins) originate from food [16]. Positive effects of the protective substances that originate from food are greater because of the synergic activity between individual antioxidant substances [16], nutritional fibrin and secondary vegetal substances in food, mainly in vegetables and fruit. Vitamin E can regenerate due to vitamin C, the later due to glutathione [16,6]. If such regeneration does not occur, the oxidized versions of the previously mentioned antioxidants can cause unwanted pro-oxidative effects and damage in cells [6,16]. These unwanted effects can potentially occur with the excessive intake of an individual antioxidant.

Results of basic researches discovered an important role of vitamins in the pathophysiology of diseases connected with oxidative stress such as: arteriosclerosis, hypertension, cataract, rheumatic arthritis, malign diseases, Parkinson's and Azheimer's diseases.

rH – indicator of hydrogen content

Every endogenous antioxidant neutralizes one free radical by donating one electron or H^- (Figure 1). With that purpose we selected, as an indicator of antioxidant potential of drinks, the indicator of hydrogen content in a biological environment expressed as partial pressure of hydrogen (rH or rH_2). rH is the "absolute indicator of the reductive potential" of a substance [17]. It shows the quantity of ions of active hydrogen in solutions, of either organic or inorganic origin. Levels of rH are mostly between 0 and 42. Level 42 means dissolved oxygen saturation rate, when the level of rH is 1, it means that the substance is rich with hy-

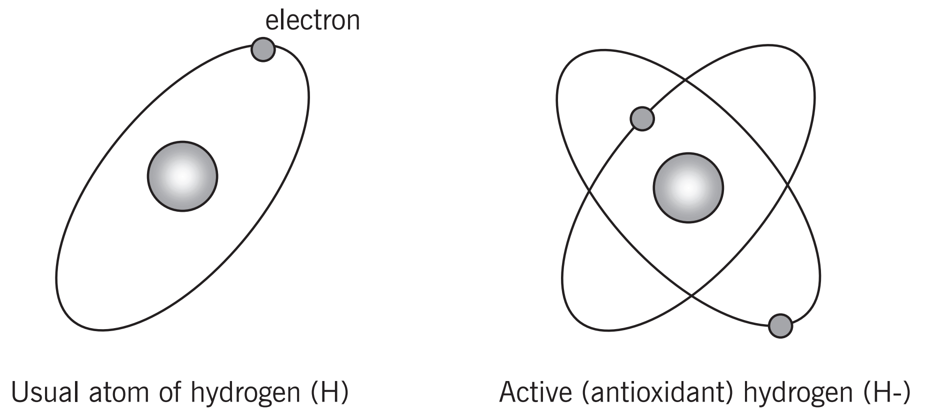


Figure 1.

Active hydrogen. Hydrogen is the smallest existing atom. Usually includes one proton that composes the core and one electron that circulates around it. In particular circumstances the atom is capable of retaining an extra electron. In literature it is called "active" or "anion" hydrogen, because it is the base of all antioxidant processes in the body and it is also called "antioxidant" hydrogen.

drogen. At this level there is no free oxygen left [17]. It is possible to obtain lower or even negative levels of rH, which represents even greater concentrations of active hydrogen. The maximum level is 28, what is above 28 means oxidization (predomination of oxidizing agents), while levels below 28 mean reduction (predomination of reducing agents).

Biological environment must be in a reduced form, thus levels of rH in biological liquids must contain greater values of hydrogen than oxygen, therefore the level of rH must be considerably below 28. The increase of rH of one unit namely means a 10 times lowering of the quantity of active hydrogen ions [17].

The purpose of this research is to determine the share of active hydrogen in natural food sources-fruit juices and teas. For these reason a relatively simple, but sensitive method that quantifies the antioxidant capacity of beverages was introduced.

METHODS

For the measurement of oxidation-reduction potential (ORP) and pH levels the simultaneous use of three instruments was performed: namely Inolab WTW pH meter, HACH Sension pH meter, HACH Sension ORP meter and Greisinger electronic ORP meter. All measurements were performed in a 100 mL cup, previously mixed, at room temperature 25 °C. The final measured levels of pH and ORP were read in mV.

The criterion for the reaction capability of a compound are oxidization/reduction potentials in mV. Reduction potential (also known as redox potential, oxidation/reduction potential or ORP) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. pH of the solution is the criterion of concentration of free positive hydrogen ions in the solution. The use of rH gives a hydrogen proton-unbiased look at the absolute reducing potential of a compound, eliminating the effect of pH in the ORP measurement. It is a true indication of a compounds reduction potential capacity. The shifts in rH can be used to quantify the reducing ability and energy reserves of the compound. The rH level is the criterion for the state of reduction or oxidation in which is the compound, it is also the indicator of the probability that the compound will react with the free radical. The direct use of pH and reduction potential measurements (ORP) gives an indication of the probability of a compound to act as an antioxidant [21,22].

Nerst equation and rH

Because of the interaction of protons at the changes of pH oxidation-reduction potential may be biased by the pH and vice versa. For this reason the variation of Nernst equation (Equation 1) was used, which is an effective way for measuring the reductive potential of a compound, which is given by the level of rH. This is the logarithmic value and is the criterion for absolute reductive potential.

$$E_h = 1{,}23 - \frac{RT}{F}\,\mathrm{pH} - \frac{RT}{4F}\ln\frac{1}{P_0} \qquad (1)$$

E_h in the equation is the measured reductive potential (mV), F is the Faraday constant (the charge per a mole of electrons), equal to $9.6485309 \cdot 10^4$ C mol^{-1}, R is the universal gas constant, equal to 8.314510 J·K^{-1}·mol^{-1} and T is the temperature in Kelvin. (Kelvin = 273.15 °C). The value 1.23 in the equation is the potential of oxygen at one atmosphere (101.235 kPa) 1.23 V higher than in the compound at the same pH. The level of rH is explicitly defined as the negativelogarithm of oxygen pressure, P_o (equation 2).

$$\mathrm{rH} = \log P_0 \qquad (2)$$

rH is the "absolute indicator of the reductive potential" of a substance [17]. It shows then concentration of active hydrogen ions, rH can be determined indirectly with the determination of ORP and pH. The formula for its reckon was already discovered in 1923 by Clark (18) (remodelled Nernsto's equation), but only in later years it is gaining full value at studying processes in living beings. Basically it is a complicated logarithmic formula, but in practice (for measurements at 25 degrees Celsius) a simplified formula is used (equation 3):

$$\mathrm{rH} = \frac{(ORP + 204)}{30} + 2 \cdot \mathrm{pH} \qquad (3)$$

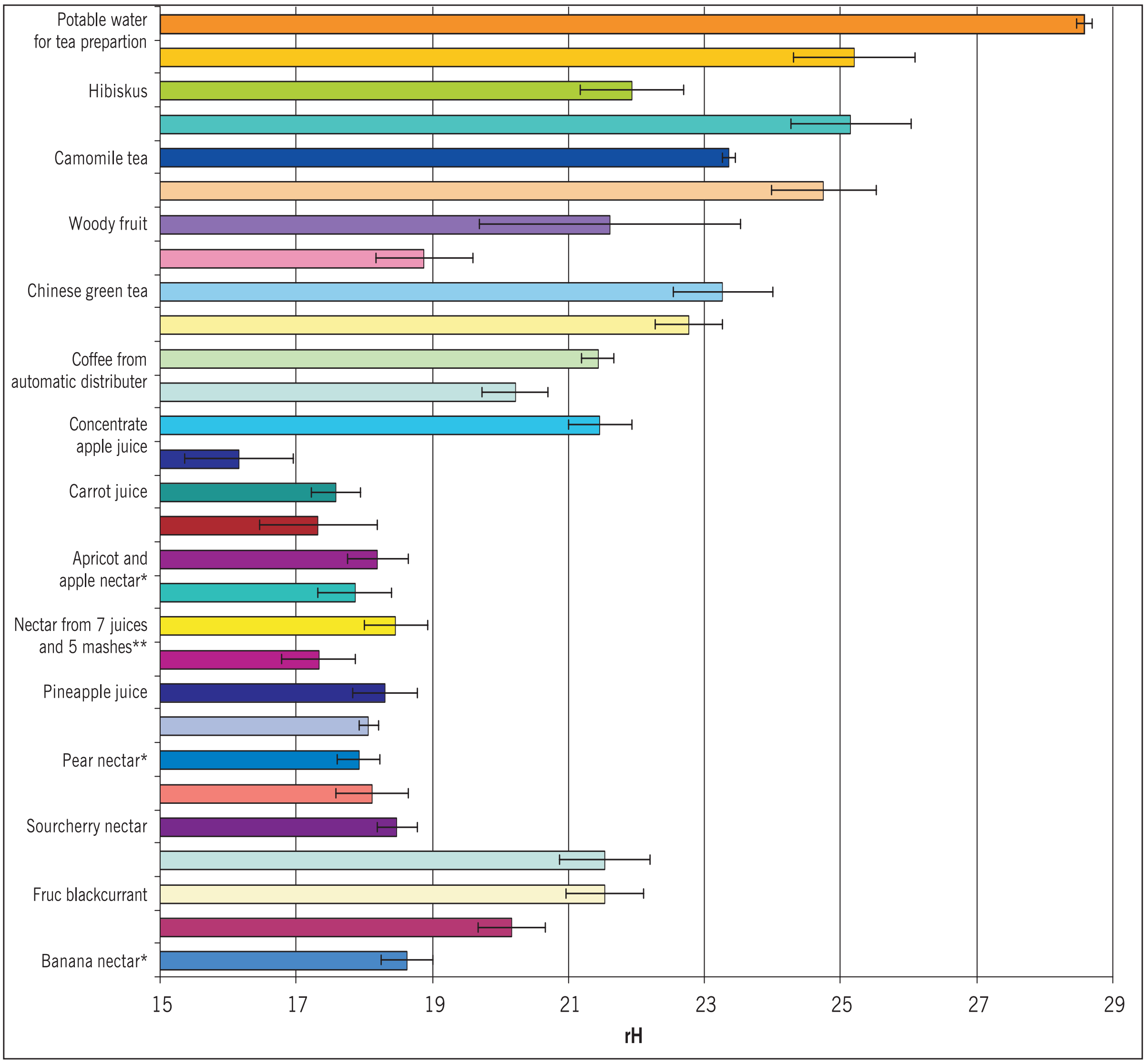
RESULTS

18 fruit juices (with different fruit/vegetable intake) and 9 teas were randomly chosen from the supermarket. Coffee was made from a public automatic distributor. In all beverages the portion of active hydrogen was determined.

The portion of active hydrogen is in all selected beverages much larger than in potable water, which is between rH=29 and rH=39. This means that all beverages have an increased value of antioxidants comparing to potable water. However the shares of active hydrogen vary significantly between singular beverages (Figure 2). This way we determined the highest value of active hydrogen in tomato juice, red grapes juice, carrot, blackcurrant, nectar of strawberry, apple and grapes, orange juice, pineapple juice, sour cherry nectar and blueberry tea. There is active hydrogen also in the pear nectar, apricot nectar, peach nectar, banana nectar, nectar made of seven juices and five mashes, but these are with added synthetic antioxidants (ascorbic acid) that contribute to the increased value of active hydrogen. The antioxidant potential of teas is lower than the antioxidant potential of the majority of juices, most likely because of different temperatures at preparation process (90 °C vs. pasteurisation). When preparing fruit juices, the pasteurization process is used for the process of heat treatment, with which pathogenic

Figure 2.

Schematic view of the portion of active hydrogen in the chosen beverages.



* added ascorbic acid (vitamin C) ** added various vitamins

micro organisms are destroyed and enzymes are inactivated for a short time at the temperature below 100 °C.

The level of rH is presented in a logarithmic scale, that means that both apple juice and coffee (both rH = 21.5) have approximately the same number of electrons in the equal unit of volume of the drink. One glass of coffee (rH = 21.5) is, for the share of H^-, almost equivalent to 10 glasses of green tea (rH = 22.7). One glass of sour cherry nectar is, for the share of electrons, approximately equivalent to 100 glasses of blueberry nectar. All juices and teas have a considerably higher share of H^- than the ordinary water from the waterworks.

DISCUSSION AND CONCLUSIONS

In current times due to our lifestyle, industrial pollution, climatic changes, overpopulation, countless vehicles, increased UV-radiation because of ozone layer depletion, cigarette smoke, infections, unhealthy way of living – human population is constantly exposed to free radical formation and all this causes increased “oxidative stress” in our bodies and related diseases in the population. The most frequent cause for oxidative stress formation is certainly cigarette smoke, which causes degenerative diseases and premature death.

A healthy adult person does not need additional vitamin and mineral supplements if he eats varied diverse food with a sufficient energy intake. However present ways of processing food led to a point where food products are impoverished of minerals and vitamins. Due to intense farming, soil is lacking minerals, because of transport fruit is picked up unripe, however it is known that antioxidants synthesize only at ripening [6], because plants use them to protect from the environmental effects (UV-radiation), diseases, pest and other stressful factors [23]. Furthermore, fruit is sprayed with pesticides that can extinguish the beneficent characteristics of protective substances in fruit. Unsuitable mechanical preparation and heat treatment can greatly decrease the nutritive value of a food product and affect the change of antioxidant potential of food [24]. The majority of Slovenians do not daily consume five portions of fruit and vegetables. Data from the research “Risk factors for contagious diseases between adult residents of Slovenia“ [25] show that 31.6 % of adults in Slovenia do not eat vegetables daily and 43.0 % do not eat fruit daily. 21.9 % of the inquired in this research, eat vegetables several times a day and 31.1 % eat fruit several times a day.

A healthy adult person does not need additional vitamin and mineral supplements if he eats varied diverse food with a sufficient energy intake.

All this states are in favour of additional intake of minerals and vitamins, which can be accomplished with increased regular consumption of fresh and raw fruit and vegetables and their juices. It has to be realized that the use of synthetic vitamin supplements is not an alternative to regular consumption of fruit and vegetables. Fruit contains thousands of compounds with unknown effects on health. Probably many antioxidants are still undiscovered, furthermore the combination of antioxidants in fruit and vegetables is optimal, as it causes their reciprocal regeneration and consecutively intensifies their defence from free radicals. Compared to vitamin and mineral supplements the advantage of consuming natural food products is in their complex and balanced content of macro and micro nutrients that enable a harmonious effect of separate active substances and consecutively less probabilities for over consumption of active components [24].

Since endogenous free radical formation cannot be deliberately increased, all we can do is increase the level of exogenous antioxidant protection of our bodies by intake of antioxidants from food, namely fruit, vegetable and their juices and teas. In the present analyze we confirmed increased amount of active H in all drinks tested as compared to potable water; with great difference between particular type of drink. The highest value of active hydrogen was in tomato juice, red grapes juice, carrot, blackcurrant, nectar of strawberry, apple and grapes, orange juice, pineapple juice, sour cherry nectar and blueberry tea. However, the greatest amount of active H was still in the two freshly prepared juices tested – orange juice (rH = 13.8) and pineapple juice (rH = 16.7) indicating that by industrial juice preparation and during the storage some antioxidant potential is lost.

It is evident that the antioxidant potential of a drink is useful and important information for consumers and should be written on the product label.

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