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From Knowledge to Wisdom

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Occurrence of Ibuprofen in the Waters of the Bengal River in Nova Friburgo

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Abstract: The increasing use of pharmaceuticals throughout the world is generating a new environmental problem where they are found in low concentrations, but the long-term risks to various organisms, as well as human health, are not yet known. These drugs, as well as their metabolites, are introduced into aquatic environments through excretions or discharges and may cause the same exposure as POPs (Persistent Organic Pollutants) due to its continued entry into the environment. The aim of this work is to develop a sensitive analytical method for the detection of ibuprofen and its metabolites in the Bengalas river that crosses the city of Nova Friburgo in the state of Rio de Janeiro. Three collection points were analyzed monthly in the river from its source, as well as points of treated water throughout the city. The samples were collected monthly and lyophilized. Subsequently, they were subjected to a solid phase extraction (silica) with the solvent dichloromethane: hexane (1:1; v/v). The samples were evaporated over a nitrogen atmosphere and subjected to a LC-MS (Liquid Chromatography with Mass Spectrometry) with 5% acetic acid gradient: acetonitrile as the mobile phase. In the search for drugs, there were found ions and fragments of ibuprofen (m/z 206, 205, 177) that were sought and compared to with their standard. These indicators can result in deleterious effects on aquatic life in these bodies of water, as well as on those who use this water from the Bengalas river.

Key words: Ibuprofen, Bengalas river, pharmaceuticals.

1. Introduction

Pharmaceuticals, personal care products and illicit drugs have been considered as emerging environmental pollutants that persist in freshwater natural resources [1]. These organic pollutants enter the water systems from various sources such as human excretion (sewage), illicit disposal, landfill leakage, water drainage or industries [2]. Several studies report that these substances are present in low concentrations (ng/L, μg/L) and that the level of these compounds present in water can cause undesirable physiological effects, both in animals and humans, acting as endocrine disrupters [3].

The city of Nova Friburgo is in the mountainous region of the state of Rio de Janeiro and has a population of 150 thousand people. The municipality of Nova Friburgo is bathed by the Rio Grande, Rio Bengalas, Ribeirao de Sao Jose and Captain and Rio Macae basins. The main rivers that cut the center of the city are the Saint Anthony river, Rio Canon and the Bengalas river, that forms after the meeting of these rivers. The city presents some hospitals and public health posts in which there are several standardized medications that are used by the population of the region and one of them is the ibuprofen [4].

Pharmaceuticals are known as chemicals of environmental concern due to health risks associated with exposure of aquatic life to these compounds and possible risks to human health when they reach drinking water, therefore, water sources should be monitored regularly [5]. Several authors have reported the occurrence of pharmaceutical residues in waters in Europe, Asia and the USA [6], but there is limited information about their occurrence in Brazil water bodies.

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Ibuprofen known as a non-steroidal anti-inflammatory drug has been widely used in the treatment of pain and inflammation in rheumatic disease and other disorders of skeletal muscle [7]. There is evidence that intrauterine exposure causes congenital malformation, such as cryptorchidism (absence of testis in the scrotal sac) and hypospadias (melting defect of the midline of the male ventral urethra) [8].

The objective of this study was to investigate the presence of ibuprofen in the Bengalas river, in the municipality of Nova Friburgo, state of Rio de Janeiro.

2. Material and Methods

2.1 Sample Collection

Samples of the waters of the Bengalas river were collected in the city of Nova Friburgo (RJ) at three points, named A (nascent; PT1 (Point 1)), B (inside the city; PT2) and C (final city; PT3), from October to December 2017. Afterwards, they were taken to the NUMPEX Laboratory of the Federal University of Rio de Janeiro, Campus Xerem, in Duque de Caxias. These were lyophilized (Liobras Model L101) with working temperature of -55 °C.

2.2 Sample Preparation

The lyophilized residue was taken to the Radioisotope Laboratory Eduardo Pena Franco of the Federal University of Rio de Janeiro for the removal of interferents from the matrix, as well as the concentration and isolation of the analytes, solid phase extraction was performed using silica gel G60, 70-230 mesh (2 g) and solvent dichloromethane: hexane (1:1; v/v; 4 mL). The resulting elute was slowly evaporated under nitrogen, yielding a solid residue which was resuspended in 1 mL of dichloromethane, then a 2 μL aliquot transferred to a 100 mL volumetric flask, and dichloromethane was added until the volume of 100 mL. From this solution, a 2 μL aliquot was withdrawn, transferred to a 100 mL volumetric flask and the volume completed. At the end of the serial dilution, a 60 μL aliquot was placed in the insert and vial for analysis.

2.3 LC-MS (Liquid Chromatography with Mass Spectrometry): Detection of Ibuprofen

Identification and quantification analysis of ibuprofen by mass-coupled high-performance liquid chromatography, Agilent 1200 series LC coupled to MS/MS quadrupole QTRAP 3200 (Applied Biosystems). The chromatographic column used was 50 × 2.1 mm C18 100A (SilaChrom). The total run time was 40 minutes, with gradients being 95% H_2O and 5% ACN (Acetonitrile) from 0 to 25 min, 10% H_2O and 90% ACN from 25 to 37 min, 95% H_2O and 5% ACN from 37 to 40 min, with an injection volume of 10 μL and scanning at Q1 from 100 to 420 Da, positive mode.

3. Results and Discussion

The Bengalas river is the river that crosses the city of Nova Friburgo and has tributaries of Saint Anthony and Conego rivers and belongs to the basin of the Dois Rios river (Fig. 1). Twelve municipalities are located wholly or partially in the Dois Rios river basin: Bom Jardim, Cantagalo, Carmo, Cordeiro, Dois Barras, Itauco, Macuco, Nova Friburgo, Santa Maria Magdalena, Sao Sebastiao do Alto, Trajano de Moraes and Sao Fidelis [4].

Three points were established for the collection and analysis of ibuprofen from incoming waters that are part of the Bengalas river. The location coordinates were obtained with the aid of a compass, at PT1: 22°20’40” S, 42°33’28” W; PT2: 22°17’49” S, 42°32’23” W and PT3: 22°16’3” S, 42°31’56” W.

Anti-inflammatory ibuprofen has been extensively used in recent years, and although the elimination of this substance in wastewater treatment processes is greater than 90%, the concentrations of ibuprofen and its metabolites that may be found in water may still be measurable receptors [9].

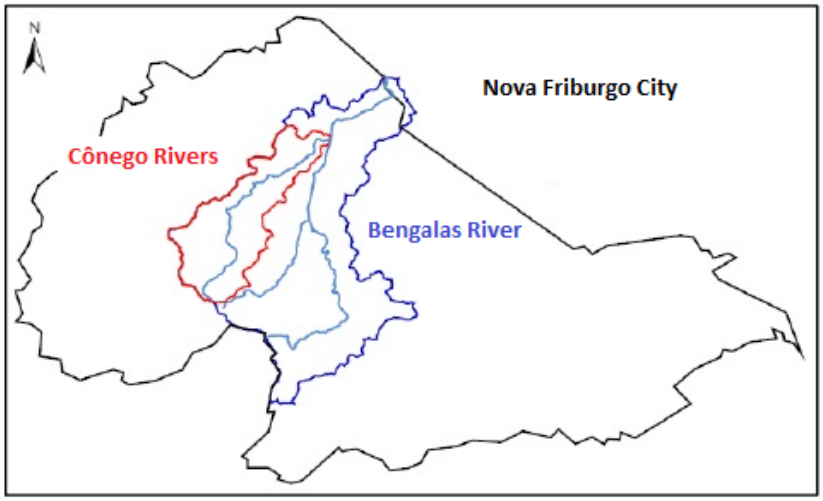

Fig. 1 Dois river basin map [4].

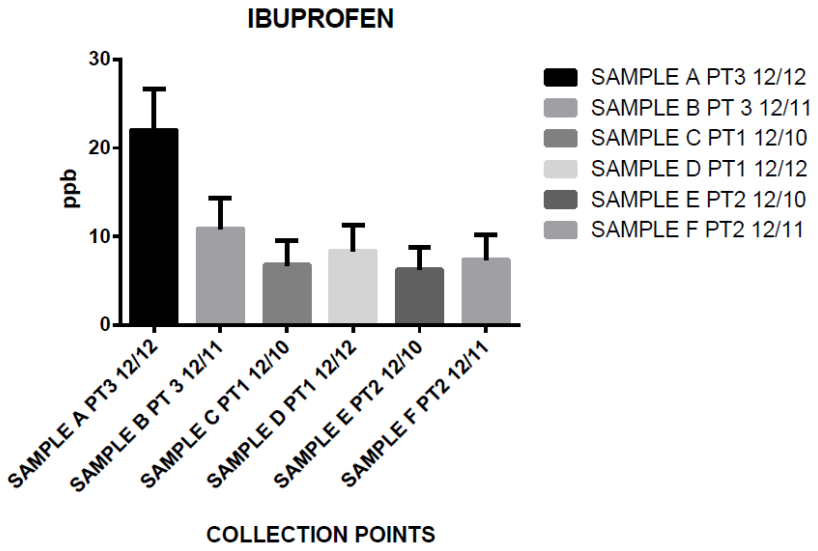

Fig. 2 Concentrations of samples in PT1, PT2 and PT3.

The total and maximum concentration of ibuprofen were verified at PT3 with approximately 20 ppb, describing the inability of wastewater treatment plants to remove complex pharmaceuticals as they were constructed with the main objective of removing carbon, nitrogen, phosphorus compounds and easily or moderately biodegradable microorganisms [10]. Fig. 2 shows the concentrations of ibuprofen in samples A, B, C, D, E and F.

Preliminary analyzes of the water collected along the Bengalas river showed the presence of ibuprofen and its metabolites, both phase I and phase II, according to Fig. 3. The mass spectrum reveals several ionic fragments, including the fraction of the metabolite derivative mono hydroxylated (m/z 221, Fig. 4), derived from ibuprofen phase I metabolism and the ion m/z 205, for ibuprofen molecule, as described by Brozinski, J. M., et al. [9].

The m/z 161, 177 fragments correspond to derivate ions of m/z 205 and 221 respectively, according to the analysis performed by Brozinski, J. M., et al. [9] (Fig. 5). The ion m/z 124 corresponds to the ionic fragment referring to the precursor 312, derived from the taurine conjugated metabolite of ibuprofen [11].

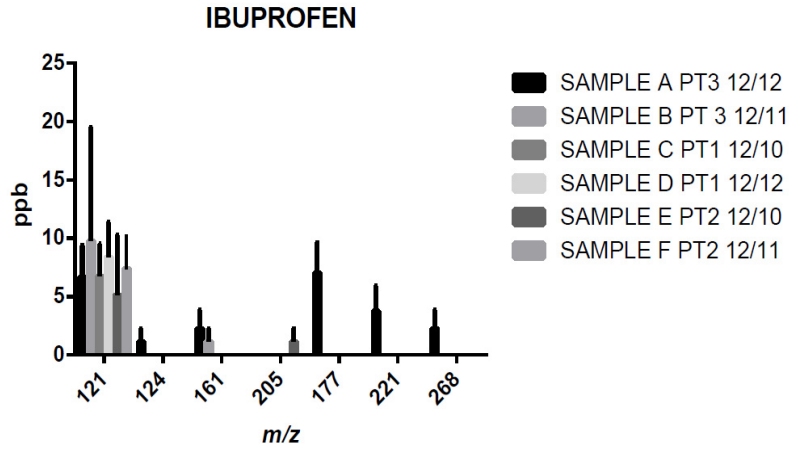

Fig. 3 **Fragments of ibuprofen and their metabolites.**

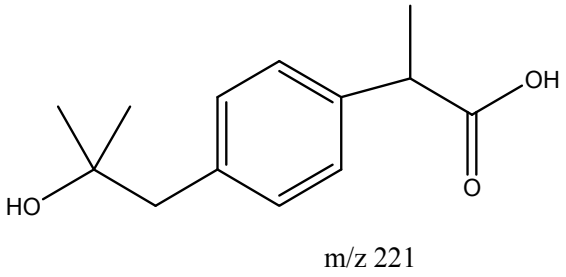

Fig. 4 **Metabolite derivative mono hydroxylated according to Brozinski, J. M., et al. [9].**

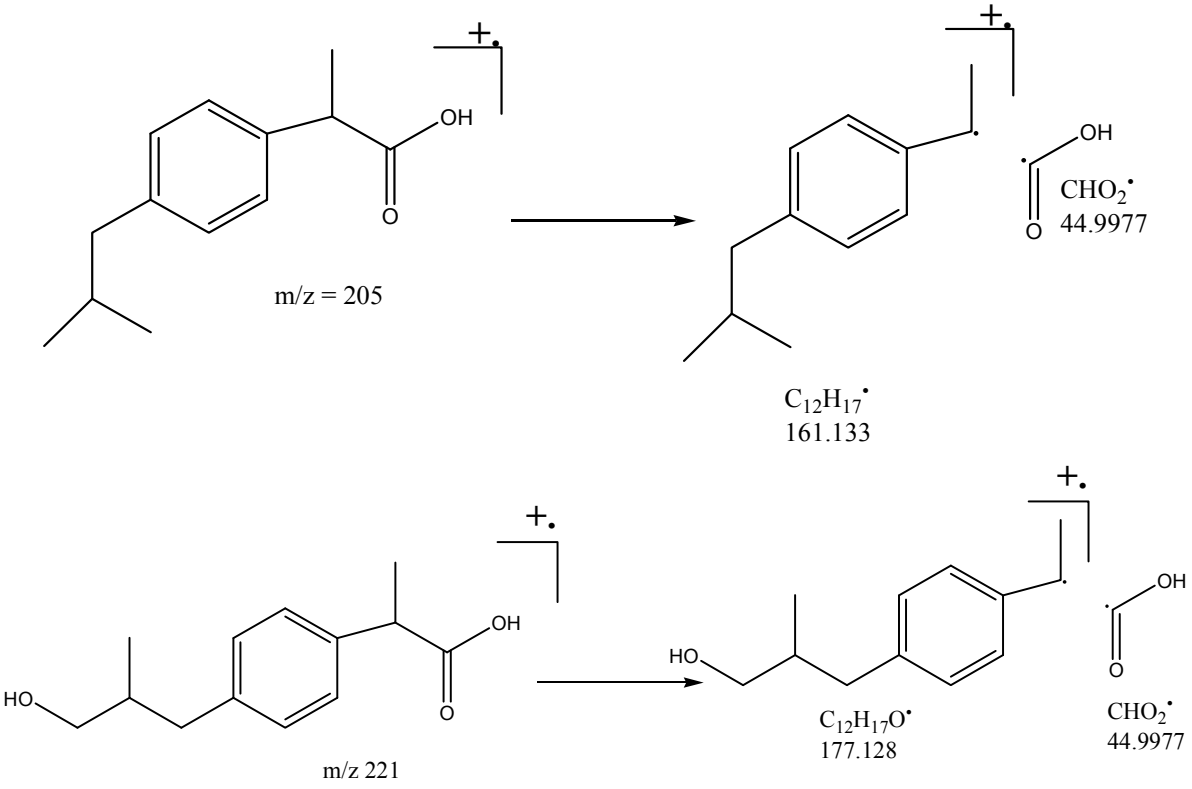

Fig. 5 **Fragments correspond to the m/z 161, 177.**

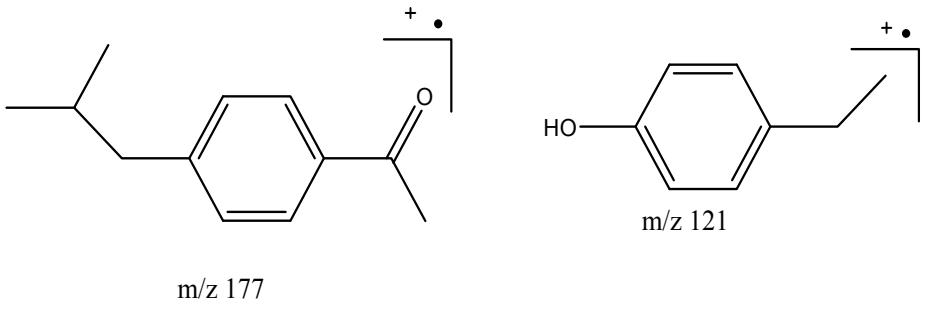

Fig. 6 The m/z 121 and 177 fragments may correspond to the oxidation products of ibuprofen [12].

According to studies by Zwiener, C. F. F. H. and Frimmel, F. H. [12], the m/z 121 and 177 fragments may correspond to the oxidation products of ibuprofen (Fig. 6).

4. Conclusion

The method was developed to study the presence of ibuprofen and its metabolites in aqueous samples, rivers and their tributaries and effluents, using the lyophilization process, solid phase extraction followed by LC-MS/MS analysis. Preliminary results showed that the concentrations of the pharmaceuticals and their metabolites can have a great impact on the ecosystem, as well as public health, considering that these substances can reach the river basins and even in low concentrations, can promote harmful health effects.

Acknowledgment

Thank CNPq for their support for project.

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Decani Bistrica River Basin Waters

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Abstract: The catchment in Republic of Kosova can be divided in basins of the rivers as: basin of White Drino in village Radavc, Peja municipality; basin of river Iber, Mitrovica municipality; basin of river Morava of Binca, Gjilani municipality and basin of river Lepenci in Kacanik municipality. The watershed subject to this paper belongs to the basin of White Drino which belongs to the Adriatic sea catchment. This river occupies nearly 6.13% of the catchment of "White Drino" and has several positive features which make it more interesting for the study such as a considerable amount of annual rainfall and a distinct topography providing strong currents. The study comprises of a detailed analysis of the quantity of water which can be accumulated and used for water supply, irrigation for agricultural, production of electric hydropower and recreation.

Key words: Catchment, river basin, stream, rainfall, utilizations of water resources.

1. Introduction

The usage of river water of Bistrica of Decani is based on the basis of the analysis for water resources management according to Eq. (1):

$$V = (L, K, Q) \quad (1)$$

where L means spatial position of the water source (km); Q means amount of water (m^3/s); K means water quality.

The analysis is made on such a way that all concerned parties for water meet their demands [1].

In Fig. 1, a general map of all Kosovo rivers is presented. The river "Lumebardhi" is one of the rivers of Kosovo, which has a fairly stable flow. The authors' opinion is that the average flow of is quite high and has a long-time duration as Eq. (2):

$$Q_{av} = 4.72\ m^3/s \quad (2)$$

Other characteristic values are in different time intervals and suitable for use as Eqs. (3) and (4) [1]:

$$Q_{min} = 0.960\ m^3/s \quad (3)$$

$$\text{And}\ \ Q_{max} = 152.2\ m^3/s \quad (4)$$

River Lumebardhi of Decani has nearly 6.13% from the surface of catchment of river White Drino. The average of rainfall perennial is $H_{sh.v.mes} = 1{,}090\ mm$ [2]. The "White Drino" stream is around 350.00 nmm, while the highest quota of basin is nearly 2,400.00 nmm.

Water demands continue to increase. Meeting the interested need for pure water is becoming more and more difficult as Kosovo's water resources are limited. Every conversation, may that be in politics, economy, culture, health or other, begins with the word water. Is there water? What is the amount of water? Will there be non-stop drinking water, water for industry, for agriculture, etc.? This is the conversation in any political presentation when there are tendencies to govern a country.

In all partisan presentation or when a political conversation takes place, it is stated or promised that the drinking water system will be constructed or improved, or the system of removing sewage or constructing facilities to protection from floods, and there will be water for drinking, irrigation, etc..

In any economy planning, the goal of having a sufficient amount of pure water is among the key priority elements which need to be secured. Then one should secure sufficient amounts and high quality water supplies for the needs of the city, industry and energy, with the exception of road infrastructure.

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Fig. 1 Classical map, Bistrica differentiated by thickness, picture of Kosovo with the river basin.

Securing sufficient and proper quality water supplies for the needs of the city impacts health and culture life, but it is also significant in terms of opportunities to develop a country's sustainable economy. A country's studies and plans of water resources are mandatory for sustainable economic plans. Without a carefully devised hydro-economic foundation, water resources of a country cannot be either preserved or utilized [3].

Water is not an everlasting asset and these resources undergo changes during global climate changes. Countries with fluctuation in the water natural balance will not have possibilities in the region as there would be an increase in the price of water and energy expenditures for using the water and there will also be additional expenditures for water quality improvements for normal economic development.

Worldwide, around 3% of the electric energy is used to bringing waters in quotas necessary for utilization.

Various measures for the improvement of the quality of water resources are necessary.

Facilities intended for water quality improvements are of varying dimensions, depending on the processes which should be performed to improve water quality. The type and dimensions of the facilities depend on physical, chemical and bacteriological features of the water as well as on the water amounts obtained for usage. For a most rational usage, several measures should be undertaken:

- Constructing high-tech equipments;
- Reducing losses in pressure;
- Reducing losses in the flow and of measures ;
- Other efficient for water usage.

Water is the element of life (Fig. 2) in all activities to lead a normal life. The country without sufficient amounts of water cannot have state independency. Water resources are a strategic element for the

Fig. 2 Photo of the river basin on the upper part of the flow.

existence of a state, therefore the increase and purification of water resources are of great importance for a society. Development of any state in the world has been closely connected to water resources. Since the ancient times water has been the dominating element in developing settlements, economies, agricultures and other.

Many preliminary studies and analyses are required when intending to use a water resource. It is necessary to have sufficient knowledge on hydrology, meteorology, topography, geology, hydrology, logical data, etc.. Based on accurate analyses conducted on these elements, it is only by using them cautiously that these resources can be used and be protected by basin waters. Special attention should be given to the ecological flow that represents the amount of water in the river for the biological needs of flora and fauna [4].

Only when information regarding the amounts of water of a basin in certain times is collected, then the water resources of a basin can be secured for a sustainable economic development, preservation of people's health, agricultural development and protection from damages from full waters.

2. Topography of the River

Decani Bistrica is located in the south-western part of the Republic of Kosova. It is a part of the White Drino river basin as shown in Fig. 3.

The source of this river originated from the 'Accursed Mountains' and starts at the 2,600 quota (Kozhnieri Mountain) and flows into White Drino at the quota of 427.

The basin of this river is $P = 269.90\ \text{km}^2$ where nearly 30.02 km^2 are agricultural fields and pastures 69.93 km^2, forests nearly 98.70 km^2 and bushes 71.60 km^2 [5].

In a longitudinal aspect, this river has a highly strong current, particularly on its upper flow as it is shown in Fig. 4.

The basin has the shape of the "leaf". Rainfalls differ greatly on its upper part of the flow compared with its lower flow. Around 60% the surface of the basin is covered with various trees. The other part of the river is pasture and agricultural land. The basin has a significant descent from and rainfalls have created the numerous streams. As the climate stretching over the river basin has significant variations during the seasons, consequently there is plenty of granulated rock as shown in Fig. 5 and when full waters appear, there is also a large carriage as shown in Fig. 6 and thus the middle and lower part of the flow, there are damages of agricultural areas.

The Decani Bistrica river has a highly rapid flow. On its upper flow, it has a descent of $1 > 8.0\%$; on its middle flow, it has a descent of $1.0\% < J2 < 8.0\%$; and the descent in the lower part of the flow nears at Eq. (5):

$$J3 < 1.0\% \tag{5}$$

The average steepness of Decani Bistrica river is as Eqs. (6) and (7):

$$S = \frac{\Delta H}{L} = \frac{(2600-427)}{52} = 41.78\, m/km \tag{6}$$

$$\mathrm{J_{av}} = 4.178\% \tag{7}$$

The average steepness of the river is 4.178%, but at its upper flow, the river has a greater steepness than in the lower or middle flow. Consequently, during rainfalls, one can observe a carriage of solid materials and their deposit along the banks but also on the surface of agricultural lands.

Fig. 3 Ground water bodies in the White Drino basin.

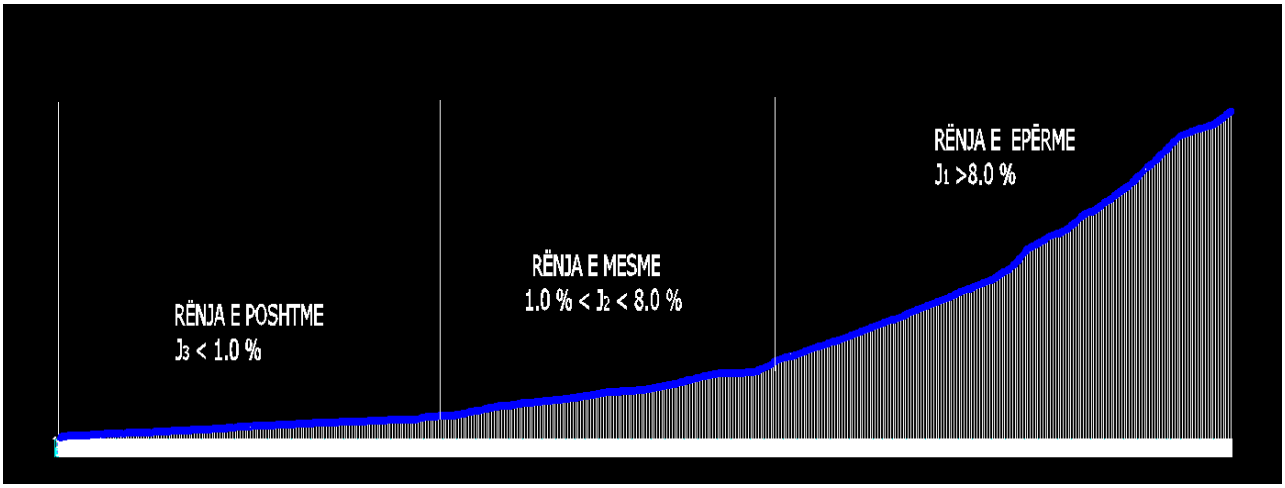

Fig. 4 The longitudinal profile of Decani Bistrica river.

Fig. 5 Photo of the river bed during the minimal flow of the river.

Fig. 6 Photo of the river Decani Bistrica on its minimal influx Q_{min}.

3. Hydrology

A station for measuring the river influx is located in the river. It includes approximately 114 km^2 or 42% of the total surface area; the measuring station is installed at 675.19 quota which was first installed in year 1953.

It is mentioned that the river has only one point of recording the influx (refer to Fig. 7).

This spot is located at the 30th km, which has approximately 42% of the water-collecting surface. There is no other profile even though authors consider the surface area of 42% to be very small in comparison to that of total surface area of the basin and other points ought to be installed in order to perform accurate influx measurements.

The water-collector of the Decani river is "leaf"-shaped which runs from the mountains of Kozhneri at the 2,253 quota and flows into White Drino at the 427 quota.

Measurements have been recorded since 1953, but there have been intermittent interruptions.

The average flow is as Eq. (8):

$$Q_{av} = 4.72\, m^3/s \quad (8)$$

Meanwhile, based on mathematical calculation, according to Gumbel's distribution, Eqs. (9)-(12) come up with:

$$Q_{\max 50\ years} = 90\, m^3/s \quad (9)$$

Whereas

$$Q_{90,100\ years} = 123\, m^3/s \quad (10)$$

$$Q_{50,\%100\ years} = 163\, m^3/s \quad (11)$$

$$Q_{90\%\ 100\ years} = 277\, m^3/s \quad (12)$$

At certain moments, the river records very high influx volume. Ground water and melted snow dominate the hydrological regime [6].

4. Meteorology

Meteorology stations to record rainfalls and temperatures are also installed in the region of Decani Bistrica.

This river has $F = 114.6\, km^2$ with a longitude $L = 52\, km$. The distance from the center of the water collector is 9 km and the concentration factor is as Eq. (13):

$$K = 2F/04 = 0.49 \quad (13)$$

and the average descent is as Eq. (14):

$$S = \frac{\Delta H}{L} = \frac{(2600-427)}{52} = 41.78\, m/km \quad (14).$$

At the inflow of Decani Bistrica, based on measurements, the rainfall values are:

Average annual amount of rainfalls for a dry year is 870 mm/y;

Average annual amount of rainfalls for year with average humidity is 1,090 mm/y [7];

Average annual amount of rainfalls for a humid year is 1,090 mm/y;

Average annual amount of rainfall for a humid year is 1,295 mm/y.

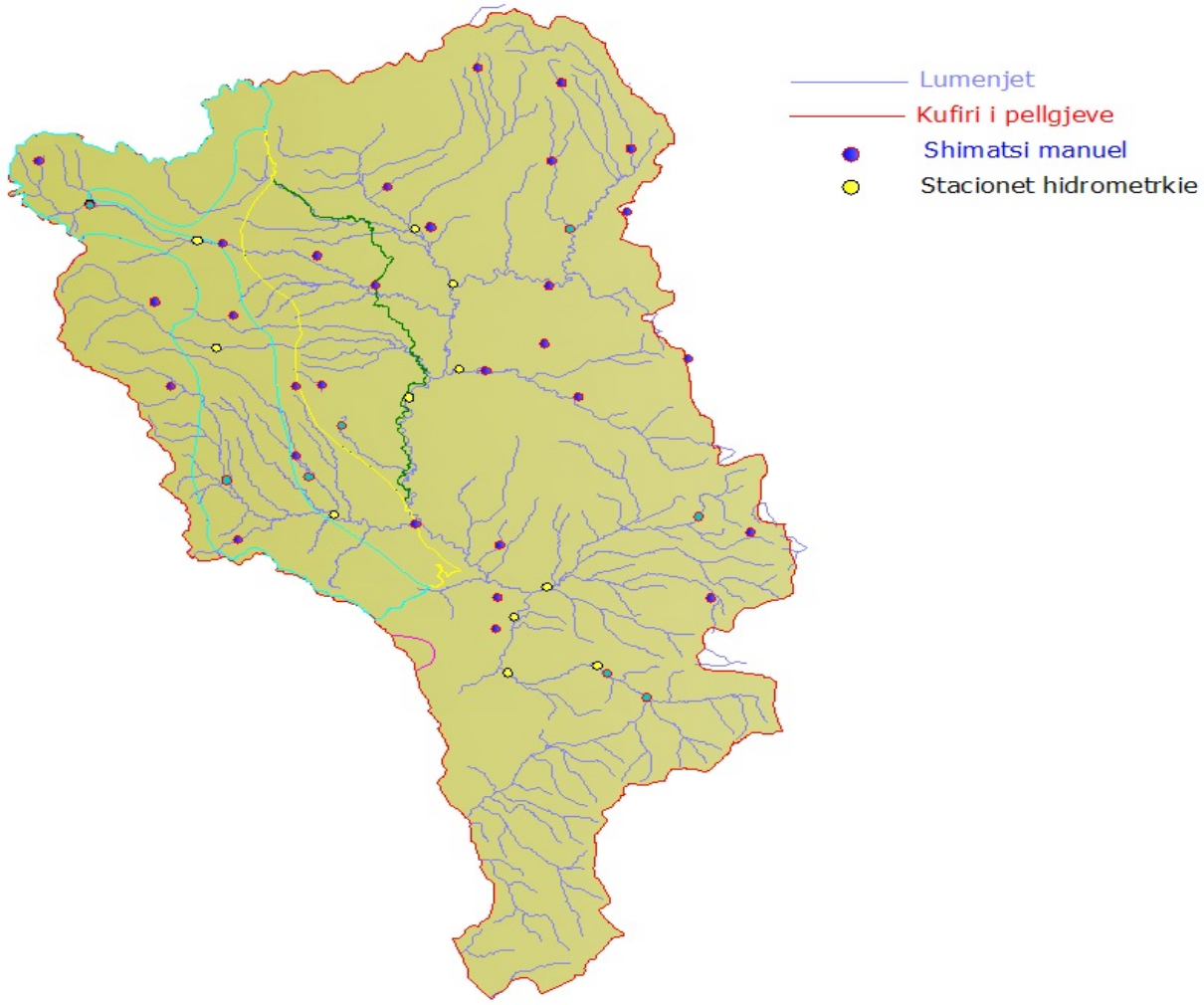

Fig. 7 Map of White Drino basin with hydrometric stations and manual rain meters [5].

Table 1 Average temperatures in Peja by season.

Winter	Spring	Summer	Autumn
1 + 1 ºC	10.9 ºC	20.4 ºC	12.1 ºC

Meanwhile, for rainfalls in the upper part of the basin are H = 1,200 mm/y in Gjakova, the nearest station. So, in year 1960, rainfall amounting at H1 = 1,600-900 mm/year have been recorded—very rich in rainfalls—a humid year, whereas for a dry year H = 1,100 mm-700 mm have been recorded [8].

Average snow days in the upper part vary from 19-12 to 25-03.

The average temperatures in Peja by season are provided in Table 1.

In the upper parts, these values are significantly lower.

5. Geology

The river basin extends at a surface areas of F = 114.6 km^2 which is covered with layers of lime rocks which destruct under the temperature's influence and then, in a form of sand, it is carried over when full waters come in [9].

Carbon rocks, lime and sedimentary rock dominate from organic remains. In the middle basin and in the lower part of the basin, there are layers of rocks and sand forms from the breakaway of lime rocks and waters carried them over when full waters came in (the melting of snow as in Fig. 8 increases the water influx). The carriage contained rocks of varying diameters over 1.0 m and sand of varying fractions.

Fig. 8 Photo of snowfalls in the upper part of the river.

6. Conclusions

The conclusions of this study can be summarized.

This study shall present an analysis of possibilities in utilizing waters of the Decani Bistrica river basin in an optimal manner. The most recent methods will be used for the analysis of most optimal solutions in the utilizations of water resources by meeting the demands of all interested for water.

Living in the century of global crisis in the world (lack of energy and water), especially in the Republic of Kosovo, the idea is to use renewable energy sources. Among of these resources is the hydro-energy of Kosovo. Therefore, it is very important to study and use it as soon as possible.

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Trace Metal Contamination of Sediments in Naviundu River Basin, Luano and Ruashi Rivers and Luwowoshi Spring in Lubumbashi City, Democratic Republic of Congo

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Abstract: As (Arsenic), Ba (Barium), Cr (Chromium), Cu (Copper), Fe (Iron), Mne (Manganese), Pb (Lead) and Zn (Zinc) concentrations were investigated in sediments collected from fifteen sampling locations in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city from February to April 2016. Chemical analyses of the samples were carried out using a portable X-ray fluorescence spectrometer. Mean pH values ranged from 4.2 to 5.8. The sediment highest mean levels of As (40 mg·kg^{-1}·dw) and Cu (3,723 mg·kg^{-1}·dw) were noted in Chemaf (Chemicals of Africa) hydrometallurgical plant effluent, those of Pb (51.5 mg·kg^{-1}·dw) and Zn (335 mg·kg^{-1}·dw) were recorded in Kabecha river and those of Ba (657.5 mg·kg^{-1}·dw), Cr (75 mg·kg^{-1}·dw), Mn (591 mg·kg^{-1}·dw) and Fe (88,450 mg·kg^{-1}·dw) were respectively found in Naviundu river at Cimenkat (Katanga's Cement factory) exit, Naviundu river under bridge on De Plaines avenue, Mukulu river and Foire channel. Mean As, Cu and Zn levels of sediments exceeded the corresponding SQGs (Sediment Quality Guidelines), PELs (Probable Effect Levels) in some of the studied rivers. They could have adverse effects on aquatic organisms in those rivers and on the health of people who depend on the rivers for water supply, irrigation and/or recreation.

Key words: Trace metals, pH, sediments, effluent, rivers, spring, Lubumbashi.

1. Introduction

Water quality deterioration from heavy metal pollution is a major issue of concern in the D.R. Congo Copperbelt, particularly given the considerable environmental legacy from 100 years of intensive industrial scale mining [1]. In the D.R. Congo Copperbelt, which includes the provinces of Upper-Katanga and Lualaba, and in other eastern D.R. Congo provinces such as Ituri, Maniema, North-Kivu, South-Kivu and Tanganyika, atmosphere, soils, surface waters, sediments and groundwater are severely contaminated with trace metals and other contaminants as a result of abandoned and ongoing artisanal and industrial mining and ore processing activities [2-9]. In many locations in those provinces, mining is typically done through artisanal mining which is a

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small scale mining method that takes place in river beds and it can be very environmentally damaging. Artisanal mining destroys landscapes and degrades riparian zones, creating erosion and heavy silting of the water [10]. Moreover, the tailings are often dumped into the rivers and could be contaminated with mercury and cyanide, thus degrading the health of the river systems and putting the wildlife and people at risk [10-12]. As sediments have a high storage capacity of chemical pollutants [10, 11], trace metals accumulated in sediments may persist in the environment long after their primary source has been removed [12] and create a potential for continued environmental degradation [7, 9-12] even where water column contaminant levels comply with established water quality criteria [11]. Indeed, resuspension events from natural or anthropogenic origin can disturb the biogeochemistry of sediments and potentially result in the remobilization of trace metals from sediment particles to the water column [7, 8, 13, 14]. Sediment-associated trace metals represent a risk for organisms living in the sediments and in the water column, especially invertebrates and fish, but also for humans through human food chain [1, 3, 8, 15-17].

The current study aims to investigate trace metal contamination of sediments in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city and to compare the sediment metal levels with the SQGs (Sediment Quality Guidelines)—TELs (Threshold Effect Levels) and PELs (Probable Effect Levels)—for freshwater sediments [18] to know the risk of the sediment trace metal toxicity to aquatic organisms. No such an assessment was previously carried out in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring.

2. Material and Methods

2.1 Study Area and Sampling Locations

The study area encompasses various water courses of Naviundu river basin as well as Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city. Luwowoshi spring is the source of Ruashi river. The Naviundu river basin includes Naviundu, Kabesha, Kalulako, Kamasaka, Ma-Vallee and Mukulu rivers, Foire channel and Chemaf (Chemicals of Africa) hydrometallurgical plant effluent. Kamasaka and Mukulu rivers are tributaries of Naviundu river which is in turn a tributary of Kafubu river. All those water courses flow through Lubumbashi, the capital city of the Upper-Katanga province in south-eastern D.R. Congo (Fig. 1).

Surface sediment samples of 25-centimeter depth were collected from twelve sampling sites in the Naviundu river basin (sample and sampling site codes 21 SD (Sediment), 22 SD, 23 SD to 32 SD) and from one site in each of Luano river (33 SD), Ruashi river (34 SD) and Luwowoshi spring (35 SD) during February, March and April 2016 sampling campaigns. Of the fifteen sampling sites, five were in Naviundu river and one in each of the other rivers, channel and effluent (Fig. 1).

The samples were collected using a sediment corer and they were stored in clean plastic bags rinsed three times with the water overlying the sediment to be sampled. A sample code as well as the sampling site and the sampling date were written on each bag containing the collected sample. To prevent the sample code, sampling site and date from being erased, a transparent plastic sticker was stuck on each plastic bag. Geographic coordinates of each sampling location were determined using a Garmin Etrex GPS and later on they were used for elaborating the map of sampling locations (Fig. 1).

2.2 Sample Preservation

After collection, the samples were immediately taken to the laboratory where they were stored in a deep freezer. Later on, they were thawed and dried in an oven at 35 °C for 5 days [19]. They were then grinded in a porcelain mortar and sieved trough a

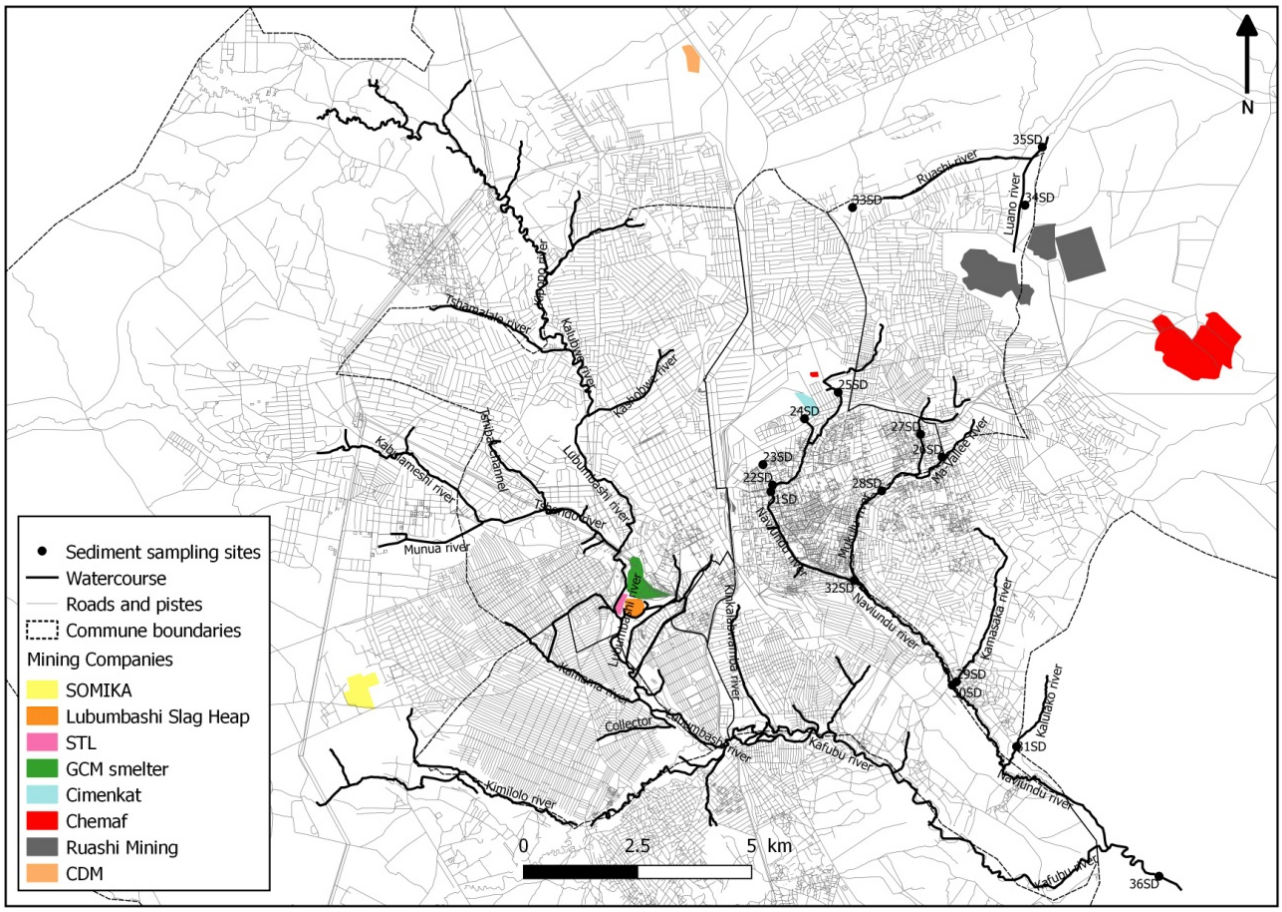

Fig. 1 Map of sediment sampling locations in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

2-mm sieve to obtain fine grain size. The grinded and sieved samples were then stored into 25-mm diameter sealed glass vials [X-RFS (X-Ray Fluorescence Spectrometer) sample cells] until they were analyzed for trace metals' content.

2.3 Analytical Method

The sediment samples were analyzed using an X-RFS. The accuracy and precision of the X-RFS measurements were evaluated by analyzing a standard reference material (soil). That indicated an acceptable quality of this method as a screening tool.

3. Results and Discussion

Mean water pH values of the sediment samples and mean concentrations of eight trace metals including As, Ba, Cr, Cu, Fe, Mn, Pb and Zn ($mg \cdot kg^{-1} \cdot dw$) at different sampling locations as well as the SQGs' TELs and PELs values [18] are presented in Table 1. Mean water pH values were very low and ranged from 4.2 to 4.9 respectively in Naviundu river at its confluence with Kamasaka river (4.2), Kalulako river (4.6), Naviundu river at the exit of Cimenkat (Katanga's Cement Factory) (4.7), Luano river (4.8) and Naviundu river at its confluence with Mukulu river (4.9) (Table 1, Fig. 2). The pH mean values were low in the other sampling locations and ranged from 5.1 to 5.8 respectively in Naviundu river under bridge on De Plaines avenue as well as Ma-Vallee river (5.1), Naviundu river under bridge on Kasenga road, Kabecha river, Kamasaka river as well as Ruashi river (5.3), Mukulu river (5.5), Foire channel (5.7) and Chemaf hydrometallurgical plant effluent as well as Luwowoshi spring (5.8) (Table 1, Fig. 2). The low pH

Table 1 Mean trace metal concentrations in sediments (mg·kg^{-1}·dw) of Naviundu river basin, Luano river, Ruashi river and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

Sampling site	Sample code	pH water	As (mg/kg/dw)	Ba (mg/kg/dw)	Cr (mg/kg/dw)	Cu (mg/kg/dw)	Mn (mg/kg/dw)	Pb (mg/kg/dw)	Zn (mg/kg/dw)	Fe (mg/kg/dw)
	SQGs									
	TELs	Na	5.9	Na	37.3	35.7	Na	35	123	Na
	PELs	Na	17.0	Na	90.0	197	Na	91.3	315	Na
Naviundu river under bridge on De Plaines avenue	21 SD	5.1	ND	542	75	ND	ND	ND	ND	39,900
Naviundu river under bridge on Kasenga road	22 SD	5.3	ND	429	ND	1,254	264	48	321	63,000
Naviundu river at Cimenkat exit	23 SD	4.7	ND	657.5	38	149.5	76.5	ND	46.5	39,050
Chemaf hydrometallurgical plant effluent	24 SD	5.8	40	216	ND	3,723	93	36	ND	59,000
Kabecha river	25 SD	5.3	20	141.5	ND	470.5	154	51.5	335	32,050
Ma-Vallee river	26 SD	5.1	ND	544.5	24	227.5	199	ND	44.5	33,000
Foire channel	27 SD	5.7	ND	591.5	ND	104	222.5	ND	36	88,450
Mukulu river	28 SD	5.5	ND	512	56	540	591	ND	71	26,700
Kamasaka river	29 SD	5.3	18	248	56	151	162	ND	ND	45,700
Naviundu river at its confluence with Kamasaka river	30 SD	4.2	ND	305.5	69	529.5	148.5	ND	232.5	20,300
Kalulako river	31 SD	4.6	ND	461.5	58.5	142.5	142.5	34	56.5	31,550
Naviundu river at its confluence with Mukulu river	32 SD	4.9	ND	431	61.5	36	82	24	33	17,650
Luano river	33 SD	5.3	ND	426.5	ND	791.5	240	ND	150.5	38,600
Ruashi river	34 SD	4.8	ND	326	69.5	762.5	221	ND	48	12,300
Luwowoshi spring	35 SD	5.8	ND	453	67	167	111	ND	ND	9,700

Chemaf: Chemicals of Africa; Cimenkat: Katanga's cement factory; dw: dry weight; Na: no available data; ND: Not Detected; PELs: Probable Effect Levels refer to concentration levels above which adverse effects are likely to occur; SD: Sediment; SQGs: Sediment Quality Guidelines (Canadian Council of Ministers of the Environment, 2001); TELs: Threshold Effect Levels represent concentrations below which a toxic effect on aquatic organisms will rarely occur.

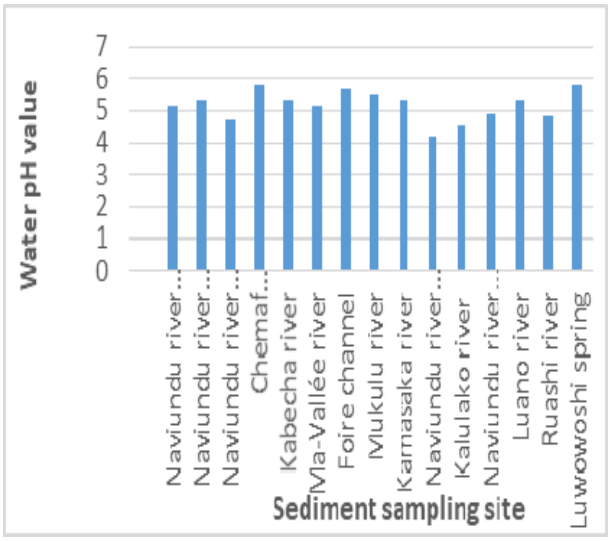

Fig. 2 Mean water pH values of sediment samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

increases metal bioavailability to aquatic organisms [6, 7, 20, 21] living in the rivers, channel and spring and to human beings who depend on those waters to meet their domestic, irrigation and recreational needs. It has been reported that mobilization of Al, Fe, Zn, Co, Pb and Cu increases with acidification and that acidification also influences the speciation of metals, transforming metals and metalloids, like As, into species much more toxic to biota [21].

Mean metal concentrations in sediments ranged from not detected in various rivers, channel and spring to 40 mg·kg^{-1}·dw in Chemaf hydrometallurgical plant effluent for As, from 141.5 mg·kg^{-1}·dw in Kabecha river to 657.5 mg·kg^{-1}·dw in Naviundu river at Cimenkat (Katanga's cement factory) exit for Ba and from not detected in Naviundu river under bridge on

Kasenga road, Chemaf hydrometallurgical plant effluent, Kabecha river, Foire channel and Luano river to 75 mg·kg^{-1}·dw in Naviundu river under bridge on De Plaines avenue for Cr. Sediment mean levels of Cu ranged from not detected in Naviundu river under bridge on De Plaines avenue to 3,723 mg·kg^{-1}·dw in Chemaf hydrometallurgical plant effluent, those of Mn from not detected in Naviundu river under bridge on De Plaines avenue to 591 mg·kg^{-1}·dw in Mukulu river, those of Pb from not detected in various rivers, channel, effluent and spring to 51.5 mg·kg^{-1}·dw in Kabecha river, those of Zn from not detected in Naviundu river under bridge on De Plaines avenue, Chemaf hydrometallurgical plant effluent, Kamasaka river and Luwowoshi spring to 335 mg·kg^{-1}·dw in Kabecha river and those of Fe ranged from 9,700 mg·kg^{-1}·dw in Luwowoshi spring to 88,450 mg·kg^{-1}·dw in Foire channel (Table 1, Figs. 3-6).

Sediment mean As levels in Chemaf hydrometallurgical plant effluent (40 mg·kg^{-1}·dw), Kabecha river (20 mg·kg^{-1}·dw) and Kamasaka river (18 mg·kg^{-1}·dw) exceeded the SQGs' PEL value (17 mg·kg^{-1}·dw), suggesting that aquatic organisms living in those effluent and rivers are at high risk related to their exposure to As. Similar As exposure risk was reported for aquatic organisms dwelling in Lubumbashi river at its confluence with Tshondo river (37 mg·kg^{-1}·dw), Munua river (29.5 mg·kg^{-1}·dw), Tshondo river (23.5 mg·kg^{-1}·dw), Kimilolo river (22 mg·kg^{-1}·dw), Kafubu river 1.36 km downward its confluence with Naviundu river (21.5 mg·kg^{-1}·dw) and Kamama river (17 mg·kg^{-1}·dw) [7]. It was reported that As can adsorb on various solid phases encountered in sediments, including aluminum, iron and manganese (hydr)-oxides, clays and organic matter and that the distribution between the liquid and the solid phases depends on arsenic concentration, arsenic speciation, competing ions, pH and adsorption properties of the solid surface, e.g. coating or isomorphic substitution [22, 23]. At pH 4, it was experimentally shown that the affinity of As(V) for several minerals decreases as follows: iron (hydr)-oxides (40 to 2,100 mmol·kg^{-1})-aluminum (hydr)-oxides (20 to 1,700 mmol·kg^{-1}) > manganese (hydr)-oxides (16 mmol·kg^{-1}) > aluminosilicates (0.4 to 0.5 mmol·kg^{-1}). The results confirmed that Fe and Al (hydr)-oxides are the main host phases for As(V) adsorption in sediments [24, 25]. Sorption processes of As(III) are more complex because $H_3As^{+III}O_3$, which is the main species at pH 5-9, is electrically neutral. As(III) essentially adsorbed on iron (hydr)-oxides, and its adsorption is not pH-dependent

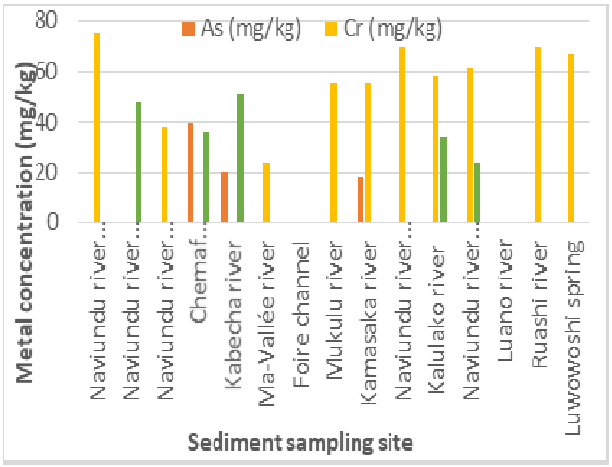

Fig. 3 Mean concentrations of As, Cr and Pb in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

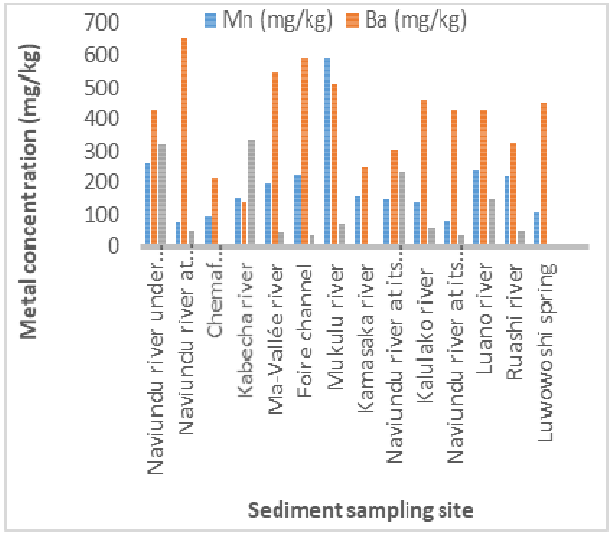

Fig. 4 Mean concentrations of Mn, Ba and Zn in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

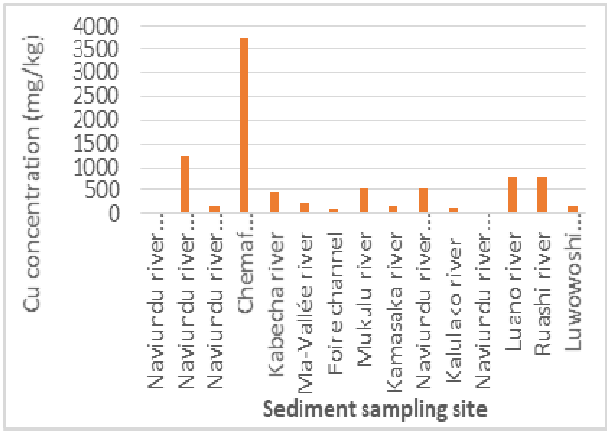

Fig. 5 Mean concentrations of Cu in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

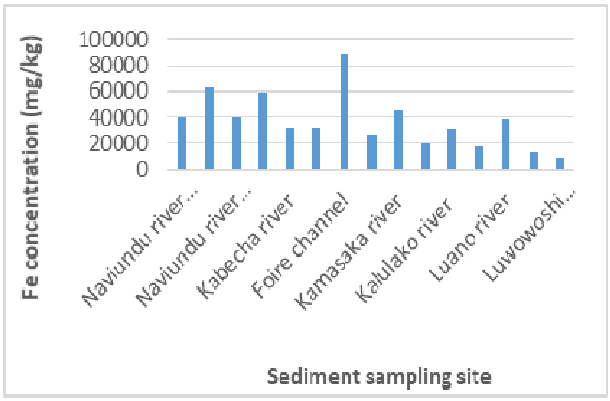

Fig. 6 Mean concentrations of Fe in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

and not as strong as As(V). It has also been shown that whatever the pH, inorganic As(V) remains the most impacted species by sorption processes with a retention capacity on minerals that decreases in acidic media [23]. Other sediment metal levels exceeding the SQGs' PELs values [18] in this study are Cu in Chemaf hydrometallurgical plant effluent (3,723 mg·kg^{-1}·dw), Naviundu river under bridge on Kasenga road (1,254 mg·kg^{-1}·dw), Luano river (791.5 mg·kg^{-1}·dw), Ruashi river (763.5 mg·kg^{-1}·dw), Mukulu river (540 mg·kg^{-1}·dw), Naviundu river at its confluence with Kamasaka river (529.5 mg·kg^{-1}·dw), Kabecha river (470.5 mg·kg^{-1}·dw) and Ma-Vallee river 227.5 mg·kg^{-1}·dw), and Zn in Kabecha river (335 mg·kg^{-1}·dw) and Naviundu river under bridge on Kasenga road (321 mg·kg^{-1}·dw) (Table 1; Figs. 4 and 5). Except Naviundu river sediments under bridge on Kasenga road, Kabecha and Luano rivers, Foire channel and Chemaf hydrometallurgical plant effluent sediments in which Cr was not detected and Ma-Vallee river sediment where Cr level was 24 mg·kg^{-1}·dw, Cr concentrations in sediments of all the other rivers were higher than the SQGs' TEL value of 37.3 mg·kg^{-1}·dw but they were lower than the PEL value of 90.0 mg·kg^{-1}·dw [18]. Pb concentrations in sediments of Kabecha river (51.5 mg·kg^{-1}·dw), Naviundu river at Cimenkat exit (48 mg·kg^{-1}·dw) and Chemaf hydrmetallurgical plant effluent (36 mg·kg^{-1}·dw) (Table 1, Fig. 3) exceeded the SQGs' TEL value of 35 mg·kg^{-1}·dw but they were lower than the SQGs' PEL value of 91.3 mg·kg^{-1} [18]. The mean concentration of Ba recorded in Kabecha river sediment (657.5 mg·kg^{-1}·dw) and that of Mn in Mukulu river sediment (591 mg·kg^{-1}·dw) in the present study were respectively higher than the highest concentrations of those metals (547 mg·kg^{-1}·dw and 531 mg·kg^{-1}·dw) respectively noted in Kinkalabwamba river and Kimilolo river sediments [7]. On the other hand, the highest Cu level of sediment in Chemaf hydrometallurgical plant effluent sediment (3,723 mg·kg^{-1}·dw), those of Cr in Naviundu river sediment under bridge on De Plaines avenue (75 mg·kg^{-1}·dw), Pb in Kabecha river (51.5 mg·kg^{-1}·dw), Zn in Kabecha river sediment (335 mg·kg^{-1}·dw) and were Fe in Foire channel were respectively lower than the levels of Cu in Lubumbashi river sediment 1.45 km downward the Lubumbashi Slag heap (5,438 mg·kg^{-1}·dw), Cr in Kinkalabwamba river sediment (174.5 mg·kg^{-1}·dw), Pb in Kafubu river sediment at its confluence with Lubumbashi river (342 mg·kg^{-1}·dw), Zn in Kafubu river sediment at its confluence with Lubumbashi river (1,534.5 mg·kg^{-1}·dw) and Fe in Kafubu river sediment 1.3 km downward its confluence with Naviundu river (108,900 mg·kg^{-1}·dw) [7]. The highest concentrations of As, Cu, Pb, Fe and

Mn in sediments in this study (Table 1, Figs. 3-6) are also lower than those respectively reported by Atibu, E. K., et al. [3] for As (54.4 $mg \cdot kg^{-1} \cdot dw$), Cu (47,468 $mg \cdot kg^{-1} \cdot dw$), Pb (851.9 $mg \cdot kg^{-1} \cdot dw$) and Fe (34,848 $mg \cdot kg^{-1} \cdot dw$) in sediments at KS-15 sampling site and Mn (1,544 $mg \cdot kg^{-1} \cdot dw$) in sediments at KS-20 sampling site of Luilu and Musonoie rivers which receive mining effluent waters. The metal contamination of sediments of various rivers, channel and effluent of the Naviundu river basin, Luwowoshi spring and Luano and Ruashi rivers might be due to atmospheric deposition, runoff from contaminated soils and urban waste discharge and mostly to effluents from artisanal and industrial processing of ores and other industrial activities in Lubumbashi city. Indeed, mining technology used in the Katanga's Copperbelt region over the past decades was not efficient and the resulting waste tailings still contained a relatively high level of metals [26]. Consequently, operators tended to "stockpile" these tailings behind small dams in valleys for later reprocessing. Meanwhile, the tailings became a constant source for releasing leached metals into surface waters, and most likely into groundwater as well [26]. It has also been reported that the exploitation of quartz and brick-making contribute to the remobilization of trace metals through the landscape, soil, air and water [27] and that during rainy season hydromorphic soils in the Lubumbashi city bottom valleys collect waste enriched with trace metals from various plants all around the city, from ore washing carried out by artisanal mining exploiters in their residential parcels, from malachite jewelry-making scattered in the city quarters and from a layer of slag spread on avenues to combat dust during dry season and mud during rainy season [28]. The metal-rich waste discharged into rivers and channel contributes to contaminate the receiving rivers and channel with trace metals. Thus, the metal contamination of waters and sediments of Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring might be partially due to urban and domestic effluents, runoff from metal-rich soils and mostly to abandoned and ongoing artisanal and industrial mining and ore processing activities in and around Lubumbashi city.

4. Conclusion

This study assessed trace metal contamination of sediments at twelve locations in Naviundu river basin and three respective locations in Luwowoshi spring, Luano and Ruashi rivers in Lubumbashi city. The results showed low mean values of water pH ranging from 4.2 to 5.8 and various concentrations of As, Ba, Cr, Cu, Fe, Mn, Pb and Zn. Chemaf hydrometallurgical plant effluent sediment had the highest As and Cu concentrations whereas the highest levels of Pb and Zn were noted in Kabecha river sediment and those of Ba, Cr, Fe and Mn were respectively found in Naviundu river under Cimenkat (Katanga's Cement Factory) exit, Naviundu river under bridge on De Plaines avenue, Foire channel and Mukulu river.

The trace metal contamination of sediments of the studied channel, effluent, rivers and spring in Lubumbashi city might be partially attributed to natural processes, unplanned urbanization and poor waste management, and mostly to abandoned and ongoing mining and ore processing activities. It presents a risk to organisms living in those sediments and in the water column and to the health of the populations who depend on those rivers, channel and spring to meet their water supply, irrigation and recreational needs.

The authors suggest that regular monitoring of the waters and sediments be carried out and that provincial and national authorities strictly apply the D.R. Congo Mining Regulations to avoid further deterioration of water and sediment quality as well as to allow full recovery of the already deteriorated water systems.

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Evaluation of Air Quality in the City of Istanbul during the Years 2013 and 2015

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Abstract: Air pollution has been the most important health issue in recent years. In this study, the aim was to evaluate the results of regular measurements of air pollutants PM10 (Particulate Matter of 10 Microns in Diameter) and SO_2 (Sulfur Dioxide) concentrations in the city of Istanbul by taking the years 2013 and 2015 as a sample. The data were obtained through the website http://www.havaizleme.gov.tr, which was published by the Administration of Marmara Clean Air Center of Ministry of Environment and Urbanization in Turkey. For the years 2013 and 2015, the mean SO_2 concentration was 8.35 ± 6.04 and 10.60 ± 7.16 μg/m^3. The mean PM10 concentration was 73.06 ± 30.63 μg/m^3 for 2013 and 51.57 ± 18.84 μg/m^3 for 2015. The acceptable upper limit values by WHO (World Health Organization) for daily mean SO_2 and PM10 concentrations respectively are 20 μg/m^3 and 50 μg/m^3. In Istanbul, SO_2 concentrations were above the upper limit values recommended by WHO, but PM10 concentrations during 2013 and 2015 were over the recommended limit values by WHO. As the particulate matter pollution is at high concentrations during these two years, it has shown that air pollution emerges as a problem awaiting solutions in Istanbul, where is industrially intense, highly populated and also with high traffic density.

Key words: Istanbul, air pollution, PM10 (Particulate Matter of 10 Microns in Diameter), SO_2 (Sulfur Dioxide).

1. Introduction

Air is one of the most indispensable and essential substance for human life. A human-being can survive only for up to 4 minutes without breathing air. Clean air consists of 78% N_2 (Nitrogen), 20% O_2 (Oxygen), 0.9% Ar (Argon), 0.04% CO_2 (Carbon Dioxide) and very small amounts of Ne (Neon), CH_4 (Methane), He (Helium), H_2 (Hydrogen) and Kr (Krypton). About 0.25% of the atmospheric mass is water vapor. Today, pollutants originating mainly from heating, industry and traffic disrupt air quality and so cause air pollution.

Air pollution has been the most important health issue in recent years. EPA (Environmental Protection Agency) determined 6 criteria air pollutants for outdoor air. These pollutants are PM10 (Particulate Matter of 10 Microns in Diameter), CO (Carbon Monoxide), Pb (Lead), SO_2 (Sulfur Dioxide), NO_2 (Nitrogen Dioxide) and O_3 (Ozone) [1]. Nowadays, it is a well-known fact that these pollutants increase the incidence of asthma and chronic obstructive pulmonary disease [2-4].

In addition, myocardial infarction, angina pectoris and hypertension among cardiovascular diseases, also cerebrovascular diseases and associated paralyses have increased due to air pollution [5, 6]. Air pollution leads to damages in the nervous system and so causes headache and anxiety; moreover, air pollution is held responsible for the increase in some neurological diseases such as Alzheimer's and Parkinson's diseases. Air pollution has unfavorable effects on fertility and child's health, too. It gives rise to low birth weight and premature birth [7]. Besides, air pollution has been held responsible for the etiology of some cancers like breast and prostate cancer, which have been increasingly incident over the recent years [8].

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Air pollution affects the environment, human health and thus life negatively. Climate change, depletion of the ozone layer and acid rains stem from air pollution. For this reason, air pollution must be monitored with AQI (Air Quality Index). This index, which was identified by EPA (Environmental Protection Agency), has been adapted and used as "National AQI" for Turkey. AQI is calculated for five main pollutants. These pollutants are PM10, CO, SO_2, NO_2 and O_3. The AQI is calculated by using these five parameters and this index is expressed in colors: We refer the values between 0-50 green as "good"; between 51-100 yellow as "moderate"; between 101-150 orange as "sensitive"; between 151-200 red as "unhealthy". The values between 201-300 are referred as "bad" (purple), whereas the ones between 301-500 are considered "dangerous" (brown) [9]. These pollutants are measured daily at monitoring stations and their concentrations are published at the website of Turkish Ministry of Environment and Urbanization [10]. But, to make comments on results and so to benefit from them in the field of health require knowing this basic information.

In Turkey, the Ministry of Environment and Urbanization have measured all the criteria air pollutants except Pb daily in each city and in each district up to today since 2005. In Istanbul, there are 31 Air Quality Monitoring Stations at 39 districts; at some districts, more than one monitoring stations exist. Yet, there are losses at some parameters for several districts. The parameters, which are obtained most regularly, are PM10 and SO_2. In this study, our aim was to evaluate the measurement results of PM10 and SO_2 concentrations, which are regularly measured pollutants in the city of Istanbul, by sampling from the years 2013 and 2015.

2. Materials and Methods

Between the years 2013 and 2015, the air quality was audited by the Administration of MTHM (Marmara Clean Air Center). The data of Istanbul were obtained through the website acceced January 13, 2016, http://www.havaizleme.gov.tr, which was published by the Administration of Marmara Clean Air Center. The acceptable upper limits by WHO (World Health Organization) for daily average, for SO_2 and PM10 respectively are 20 μg/m^3 and 50 μg/m^3 [11]. For evaluation, the months of January, April, June and September in 2013 and 2015 were chosen since these are the months that the data were either complete or included the highest numbers of days with measurement.

Among the data of these months, the measurement results of PM10 and SO_2 were entered into SPSS (Statistical Package for the Social Sciences) for Windows, Version 21.0 registered in the name of Istanbul University and then evaluated as mean, standard deviation. The monthly mean values with each other for the same year and with the other year's equivalent monthly mean values were compared statistically. The suitability of variables for the normal distribution was examined by Kolmogorov-Smirnov test. For the variables, which are distributed normally, independent samples t test was used. For the statistical comparison of the means of more than two groups, one-way ANOVA (Analysis of Variance) test was used. $p < 0.05$ was considered significant at 95% confidence level in statistical evaluations.

3. Results and Discussion

For the years 2013 and 2015, the mean SO_2 concentration was 8.35 ± 6.04 μg/m^3 and 10.60 ± 7.16 μg/m^3. The mean PM10 concentration was 73.06 ± 30.63 μg/m^3 for 2013 and 51.57 ± 18.84 μg/m^3 for 2015. The mean concentration of PM10 was above the recommended limit values determined by WHO for both years.

For the city of Istanbul, the measurement results of mean SO_2 and PM10 concentrations in January 2013 and January 2015 was shown in Table 1, whereas the ones in April for the same years in Table 2, the ones in June for the same years in Table 3 and

the ones in September for the same years in Table 4 can be seen.

Except the mean PM10 concentration during April 2015, all of its concentrations were above the upper limit values recommended by WHO; whereas the mean SO_2 concentrations were under the upper limit values recommended by WHO throughout all of these months within these two years. Among the chosen months, SO_2 concentration was detected as the highest in 2013 during April and in 2015 during January; on the other hand, PM10 concentration was detected as the highest in 2013 during April and the highest in 2015 during September.

Table 5 shows the statistical comparison of mean concentration of SO_2 measurements during the four months observed for the year 2013 by one-way ANOVA test. Among the four months' means, there is a statistical significance at high level. The comparison of mean concentration of PM10 measurements for the year 2013 during January, April, June and September by using one-way ANOVA test can be seen in Table 6. It was detected that the measurements of mean PM10 concentrations showed a statistical significance between different months.

The statistical comparison of mean concentration of SO_2 measurements for the year 2015 during January, April, June and September by using one way ANOVA test can be seen in Table 7; there is a statistical significance at high level among the means. The statistical comparison of mean concentration of PM10 measurements for the year 2015 during January, April, June and September by using one way ANOVA test was shown in Table 8; there exists a statistical significance at high level among the means.

Table 1 The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in January 2013 and January 2015 (μg/m^3).

	n	Minimum	Maximum	Mean	Std. deviation
SO_2 (2013)	31	2.0	28.0	7.32	5.71
PM10 (2013)	31	5.0	138.0	61.90	35.70
SO_2 (2015)	31	6.0	51.0	16.94	9.84
PM10 (2015)	29	25.0	104.0	53.38	23.95

Table 2 The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in April 2013 and April 2015 (μg/m^3).

	n	Minimum	Maximum	Mean	Std. deviation
SO_2 (2013)	30	8.0	27.0	15.10	5.02
PM10 (2013)	30	29.0	189.0	86.63	37.41
SO_2 (2015)	30	3.0	15.0	7.43	2.76
PM10 (2015)	28	18.0	67.0	38.86	15.93

Table 3 The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in June 2013 and June 2015 (μg/m^3).

	n	Minimum	Maximum	Mean	Std. deviation
SO_2 (2013)	30	1.0	16.0	7.70	4.00
PM10 (2013)	27	40.0	139.0	73.26	24.19
SO_2 (2015)	30	5.0	23.0	12.17	3.71
PM10 (2015)	30	33.0	76.0	55.70	12.45

Table 4 The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in September 2013 and September 2015 (μg/m^3).

	n	Minimum	Maximum	Mean	Std. deviation
SO_2 (2013)	30	2.0	6.0	3.30	0.84
PM10 (2013)	30	50.0	105.0	70.83	14.67
SO_2 (2015)	27	2.0	9.0	5.11	1.34
PM10 (2015)	27	26.0	91.0	58.22	15.68

Table 5 The comparison of mean concentration of SO_2 measurements for the year 2013 during January, April, June and September by one way ANOVA test.

SO_2	Sum of squares	df	Mean square	F	Sig.
Between groups	2,177.4	3	725.78	38.703	.000
Within groups	2,194.1	117	18.75		
Total	4,371.4	120			

Table 6 The comparison of mean concentration of PM10 measurements for the year 2013 during January, April, June and September by one way ANOVA test.

PM10	Sum of squares	df	Mean square	F	Sig.
Between groups	9,535.6	3	3,178.52	3.614	.015
Within groups	100,253.0	114	879.41		
Total	109,788.6	117			

Table 7 The comparison of mean concentration of SO_2 measurements for the year 2015 during January, April, June and September by one way ANOVA test.

SO_2	Sum of squares	df	Mean square	F	Sig.
Between groups	2,432.2	3	810.74	25.889	.000
Within groups	3,570.1	114	31.32		
Total	6,002.3	117			

Table 8 The comparison of mean concentration of PM10 measurements for the year 2015 during January, April, June and September by one way ANOVA test.

PM 10	Sum of squares	df	Mean square	F	Sig.
Between groups	6,326.7	3	2,108.91	6.863	.000
Within groups	33,801.2	110	307.28		
Total	40,127.9	113			

Taking the results in January and September as one group called "cold seasons" and the results in April and June as another group called "hot seasons", for SO_2 concentration, a statistical significance at high level was detected in 2013 between both seasons (*t*: -6.361; *p*: 0.000); on the contrary, the same statistical difference wasn't detected for the year 2015 (*t*: 1.239; *p*: 0.218). For PM10 concentration, these values were calculated as (*t*: -2.539; *p*: 0.012) for the year 2013 and (*t*: 2.353; *p*: 0.020) for the year 2015. There was a statistical significance between summer and winter seasons in terms of air pollution. In winter, the level of air pollution was more severe than summer. PM10 seemed to play an important role in air pollution. When PM10 and SO_2 results were compared according to the districts, Uskudar was ranked first among the districts with the highest mean PM10 concentration measured 89.57 ± 64.48 μg/m^3. The district of Uskudar was followed by Aksaray (PM10 concentration measured 62.80 ± 28.66 μg/m^3), Maslak (PM10 concentration measured 59.89 ± 37.93 μg/m^3) and Alibeykoy (PM10 concentration measured 54.68 ± 28.36 μg/m^3). As seen among SO_2 measurements, it was detected that mean SO_2 measurements were even above the WHO recommended limit values in Uskudar (SO_2 concentration measured 55.91 ± 28.19 μg/m^3) and in Sultanbeyli (SO_2 concentration measured 42.87 ± 29.60 μg/m^3); on the other hand, the mean SO_2 measurements were under the limit values in other districts.

According to EEA (European Environment Agency)'s data, over 90 % of the urban population in Turkey has been exposed to PM10 at unhealthy levels [12]. Air pollution within cities is also known to have negative effects on health [13]. Among different Turkish cities, there are limited number of studies indicating the status of air pollution. The annual mean PM10 concentrations recommended are 58 μg/m^3 in

Turkey, 40 μg/m^3 in EU (European Union) and 20 μg/m^3 by WHO. According to WHO's data, the annual mean PM10 concentrations between the years 2008-2015 are 85 μg/m^3 for the world, 235 μg/m^3 for Eastern Mediterranean countries with high income, 158 μg/m^3 for Eastern Mediterranean countries with low income, 123 μg/m^3 for Southeastern Asia, 119 μg/m^3 for Africa and 104 μg/m^3 for Western Pacific Mediterranean countries with low-middle income. This value for European countries with low-middle income is 55 μg/m^3, thus the city of Istanbul is shown as "moderately polluted" on WHO's maps in terms of air quality (AQI—Yellow: between 51-100). Eastern Mediterranean and Southeastern Anatolian cities of Turkey are demonstrated as "sensitive" (AQI—Orange: between 101-150) [14]. In this study, the levels of PM10 concentrations were found to be above the recommended limit values by WHO in Istanbul during the years 2013 and 2015. No research made in Istanbul about this subject was found during literature survey. In a doctoral thesis research conducted in Kirklareli, air pollution and meteorological parameters were detected to increase the number of hospital admissions due to cardiovascular and respiratory diseases [15]. In a study conducted by Bolu, F., et al. [16] in Duzce, the annual mean PM10 concentration was found to be 106.42 ± 102 μg/m^3, whereas the annual mean SO_2 concentration was found to be 6.15 ± 5.39 μg/m^3. Air pollution occurs due to local, regional and global problems. Therefore, it is possible to take measures with multidimensional studies, industrial activities, increased level of traffic, destruction of forests, combustion of biomass and continuous energy production trigger climate change and as a result of this situation, natural disasters like sea level rise, floods, hurricanes and drought may emerge. In each country, a national air quality monitoring network should be established as it is in Turkey. So as to reduce air pollution, as society, we should use public transport, use energy-efficient appliances and energy-saving light bulbs, use clean energy such as wind, geothermal and solar energy and also organize public education on these issues.

4. Conclusions

In conclusion, the lower levels of air pollution during the summer months give rise to thought that the level of heating-based pollutants decrease and the traffic reduces relatively in the city of Istanbul during the summer months. As the particulate matter pollution is within high concentrations during these two years and throughout all the seasons, it has shown that air pollution emerges as a problem awaiting solutions in Istanbul, where is industrially intense, highly populated and also with high traffic density.

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The Appraisal of the Nyakasura Cave and Waterfall Geosite—'Amabeere ga Nyina Mwiru', Toro—Fort Portal Scenic Area, Uganda

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Abstract: The Nyakasura caves and waterfall geosite of stalagmites and stalactites (191,271 m E, 74,776 m N) locally referred to as 'Amabere ga Nyina Mwiru' is part of the Nyakasura—Fort Portal volcanic field and scenic area. The geosite is one of the country's most exciting and educative features. This geosite has been long known and several legends about it were written and taught in schools. The site is taken care of by a family of the Rubomboras in whose home is situated and also referred to as the Wonder of Uganda and named Camp Beseri. The other beautiful sites include the landscape, panorama, the calderas, lava domes, water bearing and dry craters, fauna and flora and others viewed from the Kyeganywa hill (192391, 75681; 1,594 m, 00°41'2.0682" N, 30°14'11.3244" E) in Kabarole district. The nation's capacity to strengthen geopark development lies in funding the development activities and inviting or attracting geopark expatriates as well as investors. The geopark development is fundamental for harnessing geotourism which is one of the opportunities Uganda has for achieving faster socio-economic transformation as per Uganda's Vision 2040.

Key words: Geosite, geopark, sustainable development, geotourism, geoconservation and geoeducation.

1. Introduction

Uganda is one of the five East African Community countries. The country occupies an area of 241,000 km^2 and lies in the heart of the African plateau within the African plate, a continental crust containing Archean Cratons and crossed by the equator. She has a tropical-equatoria climate in addition to a variety of landscapes and other physical features (Figs. 1a and 1b), unique flora and fauna with a breath-taking beauty which gives her another name 'The Pearl of Africa'. The income per capita is 1,300$ per annum. Uganda is endowed with impressive geological sites that are potential pro-development occurrences.

As part of the general effort to document geosites in Africa, the OAGSs (Organization of African Geological Surveys) invited the GSU (Geological Survey of Uganda) to submit information on the subject. In due course of assignment, there was increased awareness of the importance of geosites and the related concept of 'Geopark'. The Survey is currently working towards having the Nyakasura cave and waterfalls geosite pioneer in the nation's geosite recognition. The geosite comprising a cave, stalamites and stalactites is the only one of its kind in Uganda with aesthetic, scientific, cultural and other unique values. It is a natural occurrence in the volcanic hills of Toro, famous for its legendary and cultural importance. The Directorate of Geological Survey and Mines, therefore, supported the appraisal and pledge to facilitate the activities towards the enhancement of its geographical and geological character. The eventual recognition of this geosite will create public awareness of its pro development potential through the promotion of geotourism. The concepts 'geosites', 'geopark', 'geotourism' and

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Fig. 1a Caldera, lava dam lake, landscape and flora.

Fig. 1b Signage to echo camp.

'geoheritage' are new, interesting and important in geoscience and have fast developing frameworks [1-12]. Brilha, J. [2] defines a geosite as an occurrence of one or more elements of geodiversity outcropping from the action of natural processes or due to human intervention, well geographically delimited and with exceptional scientific value. Other values may also be present. Ehsan, S., et al. [8] denotes geotourim as utilization of geological heritage resources for education-based tourism-geoeducation; the site

provides a formal and informal education facility, geoconservation; protecting geosites and current geoheritage is passed on to future generations as a potential Palaeo environmental record preserved in landforms and sediments. The Nyakasura caves and waterfalls occurrence are a potential geotourism product that already protects geoheritage, sustains communities, communicates and promotes geological heritage and works with a wide range of different people. The official recognition of this geosite will promote awareness and further the understanding of the public authorities, private interests, local community and the other stake holders of the geological resource potential and its contribution to sustainable development. The Nyakasura caves geosite also known as Amabeere (breasts) caves geosite is located 8 km west of Fort Portal town off Bundibugyo road in a lovely hilly area and dotted with crater lakes. It is a limestone lain area and cave having stalagmites and stalactites. The geosite is a key feature of the proposed Western Region Geopark. The locally available information [9-12] on Uganda geosites and Uganda geoparks development which started in 2009 is found in the unpublished reports with documentation on potential geosites some of which belong to the proposed Western Region Geopark of Uganda.

A geopark approach is an appropriate sustainable development strategy that can be integrated with the other development strategies. It will be a remedy if adopted to many of the African problems of poverty, hunger, economy and development to match the Uganda Vision 2040 "*A transformed Uganda society from a peasant to a modern and prosperous country within 30 years*" [13].

2. Nyakasura Geosite Position, Location and Access

The Nyakasura geosite in Kabarole district (Fig. 1c) is 256 km from Kampala following the Kampala-Fort Portal tarmac road. There are two tarmac roads that connect from Fort Portal town to Bundibugyo (56 km) and Kasese (68 km). The geosite is located 8 km west of Fort Portal and off Bundibugyo road, branching at the Nyakasura secondary school. The site has a cave and the waterfall is seen flowing through the roof of the cave.

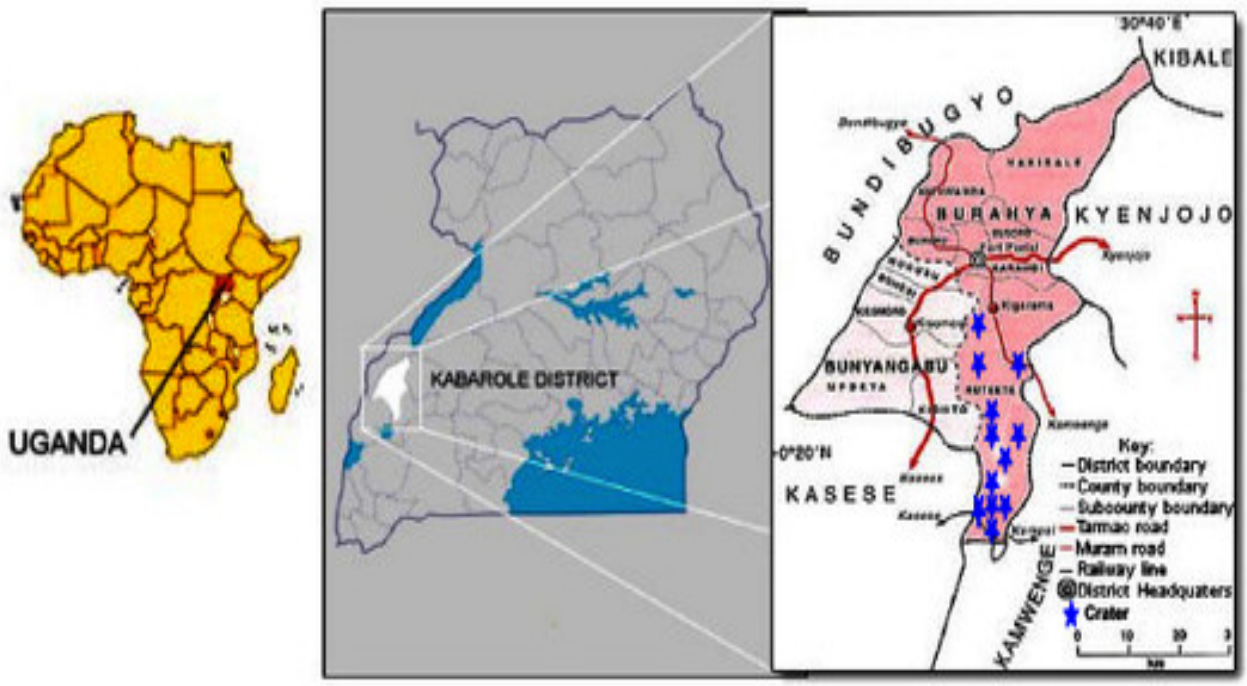

Fig. 1c Geosite positioning (Africa-East Africa-Uganda-Western Uganda).

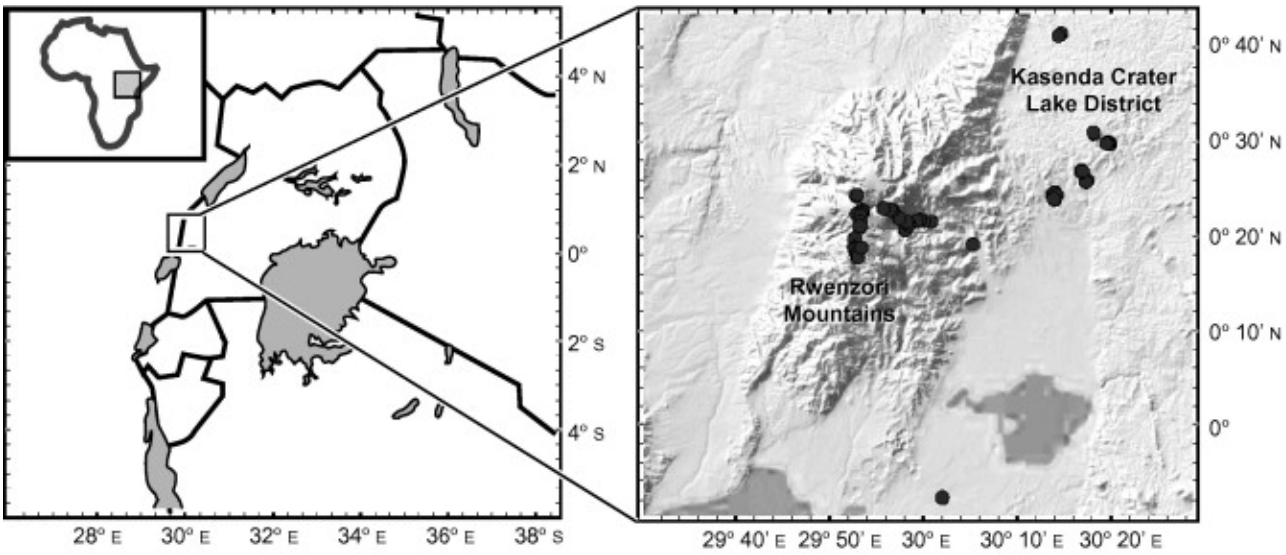

Fig. 2 Volcanic field image and its geographical position.

Fort Portal town is in both regional and strategic town categories of the Uganda vision 2040 development plan. The town is geographicaliy located by the Rwenzori mountain ranges (Fig. 2) which influences the cool nature and climate. It is close to the boarder shared with D.R. Congo. Fort Portal is ranked amongst the clean towns and has the whole range of the star hotels for accommodation. The population in the area by 2010 was estimated 452,100. The main ethnic groups are the Batoro, Batuku and Basongora and also the Bakiga, Bakonjo and Bamba. The proposed geopark is located on the Fort Portal topo degree sheet 65, a volcanic field covering the districts of Kabarore, Kasese and Bundibugyo. Fort Portal town is the major town and there are twelve other trading centers for communities within the project area. As many as 49 crater lakes and other significant geopark features exist in the Ndale area.

3. The Nyakasura Current Status, Activity, Development, Appraisal and Legend

One is guided to this site by a sign post to a reception area (Fig. 3a) at a well-established artist fabrication also very close to a permanent well looked after homestead of the Rubomboras. The maintenance and salaries for the tour guides were provided by the entrance fee of 6,000 UGX ($2) per head. There is always great feeling; a refreshing and the 'no stress' experience at the Nyakasura geosite. The geosite receives visitors through the year while November and December are as the peak season. There are organized school geography trips in which pupils visit the cave and do the hills climbing and site seeing, community interaction among others. Figs. 3a, 3b and 4 provide the general impression of the touristic resource, activities while at the highlights of one of the visits to the geosite by the appraisal team in 2016. The visitors include students, geotourists and others both local and foreign, groups and individuals on holiday, researchers from universities and geologists. Originally, this was a 'no-go' area as it is believed to be the home of the historical Chwezi kingdom. Mr. Rubombora is remembered for having braved and occupied the place and he attached value to all superstitions. The educator OB (Old Budonian) King's College Budo, Uganda and family of Batoro tribe own the land and locally do the protection by fencing the site. The Nyakasura falls and cave geosite occupies 910 acres, a private property for the Rubomboras also named Camp Beseri—Wonderland of Uganda. The family is the current management team who provide the protection status by fencing off the land with the caves. The sign

Fig. 3a Campsite reception.

Fig. 3b The Nyakasura geological touristic resources.

posts direct the visitors to the camp site and they have a reception place and tour guides. New tracks for climbing the hills, accessing the crater lakes and viewing the calderas were constructed.

The Nyakasura cave and falls geosite is included in the school geography and history syllabi taught as a physical feature of western Uganda and as a legend respectively. The legend is very interesting and has been taught in primary schools for 120 years. The cave 'Amabeere ga nyina Mwiru' (breasts of Mwiru's mother) is named after Nyinamwiru who was the daughter of Bukuku the gate keeper during the Batembuzi dynasty—predecessors of the current Babito Kings of Toro and Bunyoro kingdom. She was a beautiful girl who refused to marry the man her father chose for her. As a result, she was punished by cutting off her breasts, which then grew into rock dripping with milk. He eventually hid her away in the caves. Whilst there, Nyinamwiru was impregnated by the Batembuzi King Isaza to give birth to Ndahura, the future founder of the Bachezi dynasty. Because she had no breasts, she fed the infant with the cloudy limestone 'milk' that

drips from the breast-like stalactites. Legend has it that after, Ndahura surrendered the Bachwezi throne to his son and retired to his birthplace. Foot prints can still be reportedly be seen in the cave's vicinity. Several other legends are told about the cave. One chamber is said to have been the resting place of the Bachwezi dogs, and the ceiling shows pits resembling dog paws (Fig. 5a). The dripping water from the woman breast shaped stalactites (Fig. 5b) deposited white calcite, so the water looks whitish. This is why the local community calls it *breast milk*.

However, the guides are well educated and tell the scientific background as well as the legend.

A waterfall called Natural Shower (Fig. 5c) is said to have been used by the Bachwezi to take showers. The visitors are also allowed to do so if they wish.

Fig. 4 Appraisal visit team, 2016.

Fig. 5a Dog paws.

Fig. 5b Dripping breasts.

Fig. 5c The waterfall.

Fig. 6a Inside the cave.

Fig. 6b Visitor boot.

The Nyakasura appraisal exercise objective is to highlight the existence of the unique heritage and promotes awareness of its embedded potential as a development strategy and also to identify the problems and challenges at the site and to package for investors and seek for expert help and guidance on geosite enhancement and development. The inventorying activity of the geosites is a continuous exercise with GIS-aided data collection intended to track geotrails and route that goes through the proposed geopark. The tour involves a 3-hour walk with tour guides inside the caves (Fig. 6a) and later the other elements outside the caves which include climbing to the highest hill top and trailing the crater lakes, calderas and domes, beautiful little hills that allows one to appreciate the stress killing panorama. The caves and falls management reports a growing visitor record for the last forty years. However, the cave requires quick protection intervention from the many threats—effects of frequent earth tremors, heavy rains, heavy vegetation-eucalyptus trees on the roof of the cave and visitor walking on the growing stalagmite (Fig. 6b).

5. The Proposed Geopark Route

The geopark tour may be started with Nyakasura geosite as 'gateway' or entry point. The draft map (Fig. 7) shows one possibility of a geopark area and the GPS track record of possible route from Nyakasura—Fort Portal taking Kamwenge road through Ndale crater lakes villages. The corresponding readings of coordinates for the stops or visited sites in the geopark are listed in Table 1. The panorama, relaxing ambience,

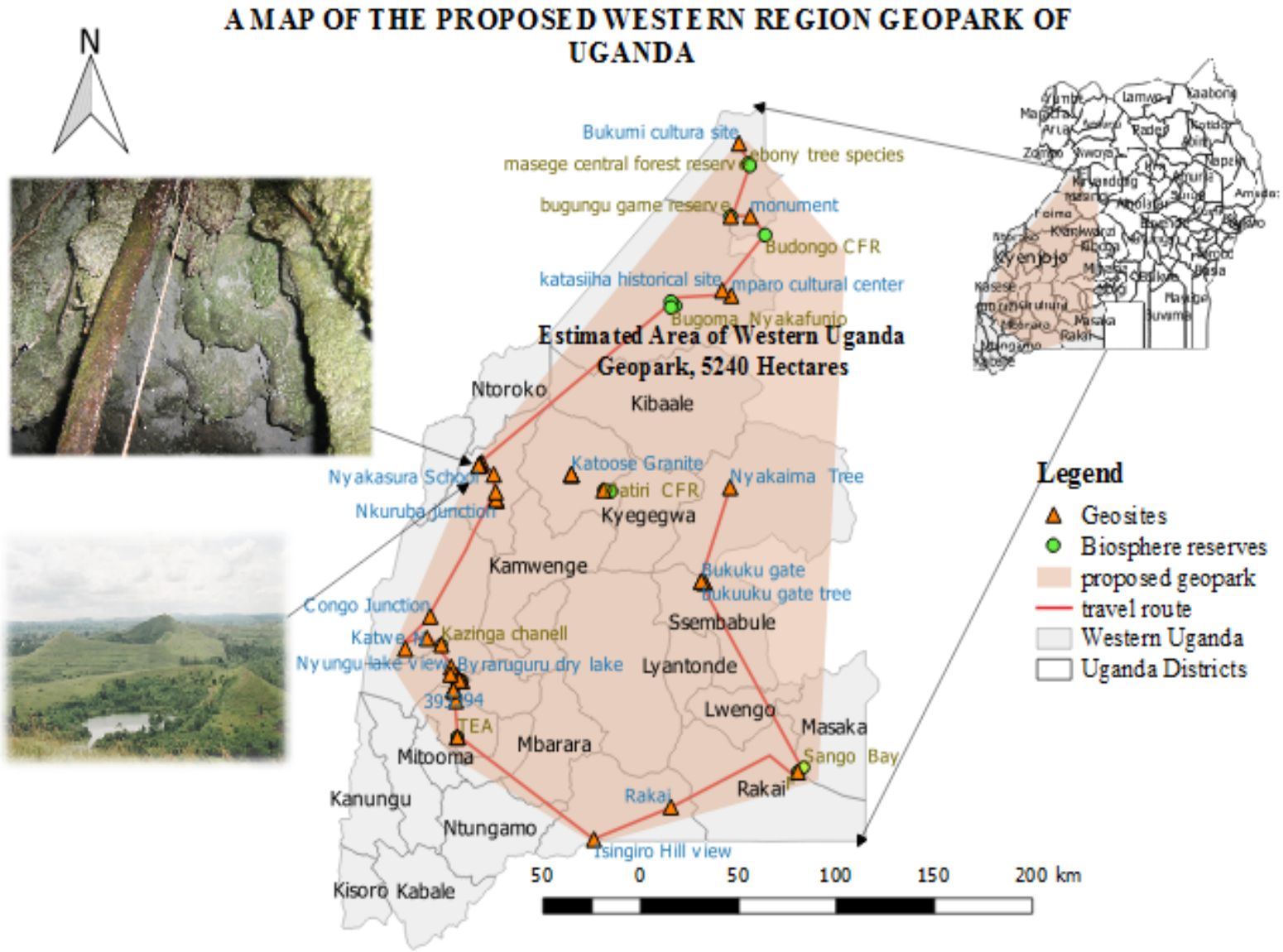

Fig. 7 Draft map showing extent and route of geopark.

Table 1 Coordinates of the visited sites in the geopark (biosphere and geosites).

Site description	Description	Easting x	Northing y	Elevation (m)	Latitude x	Longitude y	District
Katoosa central point		238,201	69,944	1,373	00°37’56.1659” N	30°38’52.0854” E	Kyenjojo
Mabeere ga Nyina Mwiru	Point 1 meeting	191,211	75,052	1,571	00°40’41.5835” N	30°13’33.2026” E	Kabarole
	lake view point	191,931	75,193	1,591	00° 40’46.1839” N	30°13’56.4678” E	Kabarole
Kyeganwa foot hills		192,391	75,681	1,594	00°41’2.0682” N	30°14’11.3244” E	Kabarole
Nyakasura school		190,722	74,356	1,565	00°40’18.9323” N	30°13’17.4127” E	Kabarole
Lake Nkuruma	junction	199,581	57,468	1,505	00°31’9.6611” N	30°18’3.9791” E	Kabarole
Lake Nkuruma camp site		199,603	57,668	1,493	00°31’16.1682” N	30°18’4.6874” E	Kabarole
L Katwe Tc		821,017	9,984,098	913	00°8’37.2731” S	29°53’1.2528” E	Kasese
Lake Katwe st		819,856	9,985,848	887	00°7’40.3519” S	29°52’23.7327” E	Kasese
Kalinzu forest reserve	stop 1	179,800	9,940,572	1,616	00°32’13.1339” S	30°7’24.7257” E	Rubirizi
	meeting pt	179,029	9,958,488	1,504	00°22’30.3362” S	30°7’0.0448” E	Rubirizi
Bunyaruguru dry wells		179,721	9,970,864	1,316	00°15’47.7648” S	30°7’22.5166” E	Rubirizi
Kashoha forest reserve		182,155	9,968,232	1,281	00°17’13.401” S	30°8’41.1433” E	Bushenyi
Nsongezi		249,746	9,890,266	1,232	00°59’31.2986” S	30°45’4.596” E	Ishingiro
Sango bay		340,567	9,931,814	1,204	00°37’0.1407” S	31°34’2.2215” E	Rakai
Bigo bya Mugenyi shrine		306,255	16,963	1,227	00°9’12.2338” N	31°15’32.854” E	Ssembabule
Bukuuku gate tree		304,681	17,343	1,104	00°9’24.6005” N	31°14’41.9542” E	Ssembabule
Nyakaima tree		319,456	63,433	1,572	00°34’25.1993” N	31°22’39.4828” E	Mubende
Budongo CFR		337,380	187,832	3,587	01°41’55.7286” N	31°32’17.1464” E	Masindi
Bbugungu game reserve		319,763	197,105	807	01°46’57.1714” N	31°22’46.8972” E	Buliiasa
Bukumii Geosite extrctn of Marram		323,988	233,004	613	02°6’26.0708” N	31°25’2.5085” E	Buliiasa
Masege central forest reserve		328,834	223,013	638	02°1’0.9411” N	31°27’39.647” E	Buliiasa
Marram etraction site 2		320,422	198,156	724	01°47’31.4077” N	31°23’8.1892” E	Buliiasa
Ebony tree species		329,475	221,957	625	02°0’26.5794” N	31°28’0.4222” E	Buliiasa

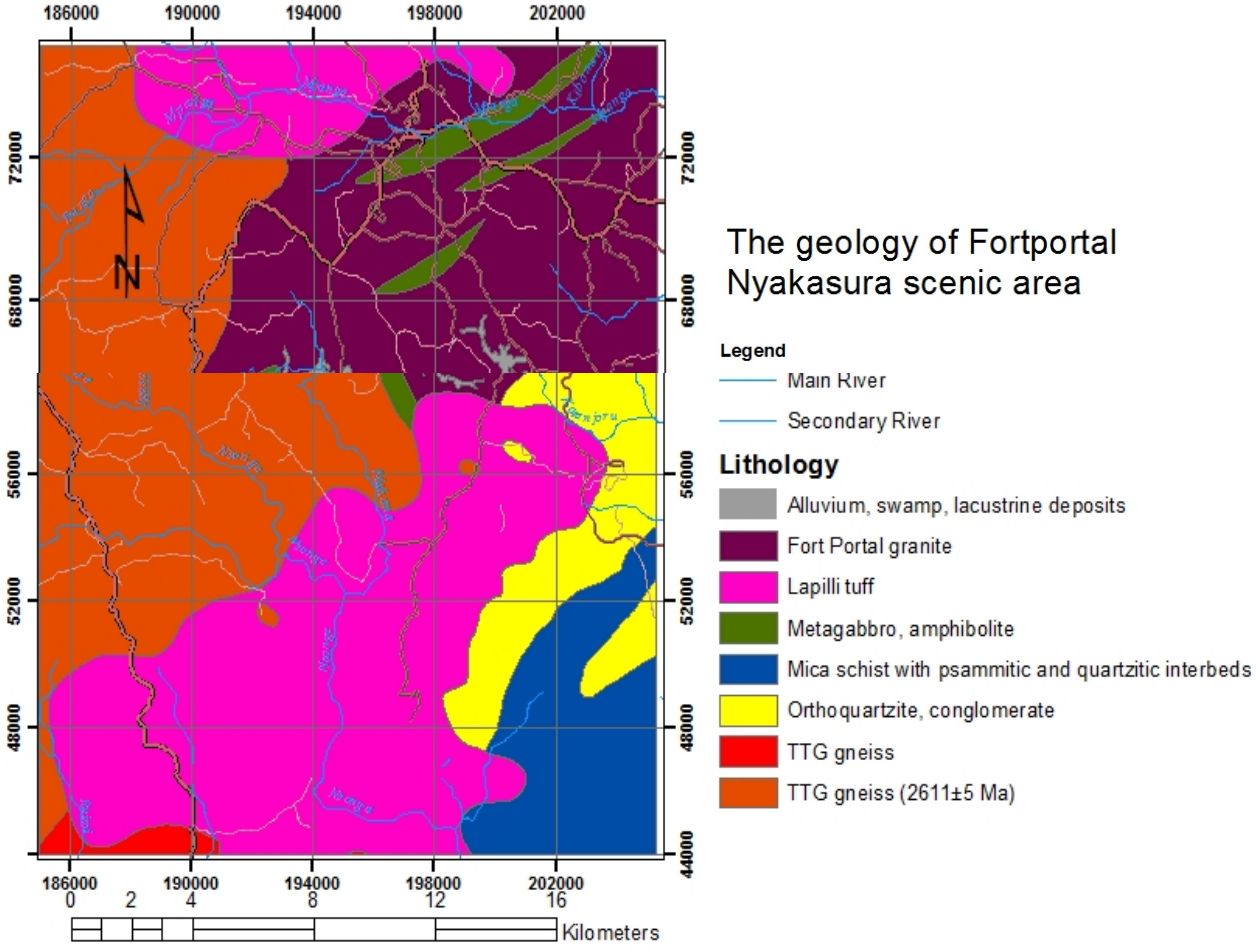

Fig. 8 The geology of the Nyakasura geosite area.

Fig. 9 Lapilli tuffs.

the banana plantations, the people and culture among others are the attractions on route. The other attractions included biotic, archeological and cultural sites biosphere reserves, the Queen Elizabeth National Park, salt production project at Katwe, lime and cement production at Hima, the west arm of the East African rift valley and others. The available hotels, motels and lodging range in stars to five star hotels.

6. The Area Geology

The area geology (Fig. 8) is dominated by volcanic Lapilli tuffs (Fig. 9) which are pale grey in colour. They occupy the hills and form the rich black soils that favour agriculture. The tuff layers range from a few centimetres close to a metre. The tuffs surround the beautiful crater lakes. The crater lakes region is underlain with the Lapilli tuffs. They are raw materials for making building blocks for many houses including those of the Rubomboras—Caves Campsite.

7. Way Forward

The Geological Surveys Department, Ministry of Energy should continue with community awareness programs on what geosites and geoparks are and their importance. The Ministry continues to receive proposals and facilitation of the geosite development activities and is financially supported. The activities include the inventorying, GPS aided tracking and making geopark map. The Ministry's main function is to create an enabling environment in order to attract investment in the development of the resource. There is need to search for and develop partnerships with investors and geosite-geopark experts. They will together supplement the technical gaps, guide on the work plan and budget for the development of the geopark and mobilize the participation of public authorities, private interests and local communities.

8. Conclusion and Recommendations

There is hope for the area developing as a result of the existence of Nyakasura geosite. The Geological Survey and Mines Department has so far contributed to the collection of geosites and a list of the geosites that exists in the country has been generated. The potential of the geosite is evident. The community begins to appreciate the importance of the geosite and would benefit from its development. Many visitors appreciate the stress-killer environment as well as learning and leisure. Training and exposure of the geosites team through refresher courses, conferences and seminars by geosite-geopark investors and experts in order to equip the members with the knowledge and skills to speed up the promotion and development of these sites. The Directorate of Geology will have contributed towards the economic growth of this country as per its mandate.

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Holland's Method as a Material in Environmental Education

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Abstract: In this work, the Holland's methodology is modified for the categorization of human personalities by including queries (in the corresponding questionnaire that serves as an evaluation tool) investigating its responders' attitude as regards his/her willingness to be professionally engaged with the natural or/and anthropogenic environment. The population used as representative sample consisted of 250 students following courses at high school and university level. The quantitative methods used were descriptive statistics, parametric and non-parametric statistics hypothesis (on causal relations) testing, categorical semantics, ontological mapping fuzzy sets and interval algebra. The results obtained showed relative significant internal consistency at macro-level for almost half of the interviewees, but the dependence of answers to environmental queries on the rest responds to the rest queries was insignificant, indicating lack of specific knowledge and clarification of the corresponding concepts at micro-level.

Key words: Environmental education, Holland's theory, questionnaire design, hypothesis testing, vocational typology.

1. Introduction

The central hypothesis in Holland's theory is that the vocational interest is a key aspect of the individual. People can be described by their degree of resemblance to six theoretical personality types: Realistic (conforming, hard-headed, practical, inflexible and un-insightful), Investigative (independent, intellectual, precise, rational and reserved), Artistic (emotional, imaginative, introspective, nonconforming and sensitive), Social (cooperative, friendly, helpful, responsible and warm), Enterprising (agreeable, ambitious, energetic, extroverted and sociable) and Conventional (conforming, conscientious, efficient, obedient and practical) [1]. Each type is characterized by distinctive preferences, outlooks, competencies and self perceptions. In practical applications, information about a person's preferences, goals and self estimates is used to assess the degree to which an individual resembles each of the six personality types; these types are not always clear and pure and a variety of mixed personalities are not uncommon. At what level of the same kind of work will influence a person is determined by one's intelligence, self-knowledge and professional information/background [2].

Environmental attitudes are conceptualized in terms of behavioral theory as being composed of beliefs towards an object [3]. The environment as an object is difficult to define; it may be an attitude object which has been forced on the respondent by journalists and researchers, but it may not make sense to respondents who see the environment much more in terms of its component parts that they personally experience. The factors that may influence one's environmental attitudes are: knowledge, background, experience, perception, values and context. Environmental concern appears to be a specific belief which is largely embedded in cognitive structures and should be considered an opinion rather than an attitude. While changes in this opinion have been documented, it is not clear that environmental attitudes or values have shifted, although attitudes have most probably become more differentiated over the last decade.

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The investigation of the attitudes of young people is very important to environmental education, whose role is to shape positive behaviors towards the environment. Linking environmental and vocational type helps grouping of personalities. The psychometric tools available in the literature are in the form of census questionnaires used to assess job characteristics [1]. In this work, the Holland's methodology is modified for the categorization of human personalities by including queries (in the corresponding questionnaire that serves as an evaluation tool) investigating its responders' attitude as regards his/her willingness to be professionally engaged with the natural or/and anthropogenic environment.

2. Methodology

It is used Holland's methodology to develop a questionnaire with 42 Likert-type questions, grouped in seven to six clusters according to Holland's vocational types [3]. Each group includes questions of vocational interest and one or two of environmental interest. The interviewees were mainly students, aged between 15 and 24, of both sexes, interviewed in person. The sample includes students of technical vocational schools and high schools, as well as, by undergraduate and post-graduate university students. Respondents filled the questionnaire by themselves at class, at the presence of their teacher/lecturer for any clarification needed. Scoring followed the five-point scale, from 1 = strongly disagree to 5 = agree completely. At the end of each questionnaire, the student had to describe himself by ranking the six personality types with descending order of preference. That gave two sets of scores (i.e., the summation of the scores that each respondent gave to the questions) on occupational preferences, one from the responses to the questions and another from his ranking preferences (initial and final, respectively). The questionnaires data were registered in excel and processed with SPSS (Statistical Package for the Social Sciences)-Statistics, using R^2, weighted rank (r_T), Pearson's, Kendall's and Spearman's coefficient correlations [4, 5].

3. Results

The survey was conducted within 20/5/2011-20/6/2011, using the high school and technical vocational schools of Zografos (east suburb of Athens) and undergraduate and post-graduate students of the University of Piraeus. Some problems have been registered during the completion of questionnaires, mainly due to miscomprehension of the questions (especially at the lower levels of education), lack of time and the influence of the classmates. The study extends to the diversification of respondents according to age, sex and educational level. The students sample consisted of the 47% women and 53% men. The distribution according to the students' origin is 40% from technical vocational schools, 42% from high schools, 7% in undergraduate university courses and 11% in post-graduate courses. The age distribution is given in Fig. 1. As regards the personality types, 12.3% of respondents belong to type A, 17.5% are registered as type B, 15.8% fit in type C, 25.7% belong to type D, 10.5% are type E and 18.1% are assigned under type F.

The correlation of personality type with the degree of environmental awareness has been used herein as a tool to determine the approach (extend, intensity and depth) that environmental education should follow on each of the six Holland's types. The most friendly type to environment is type D (Social), followed closely by type C (Artistic), type E (Enterprising), type F (Conventional), type B (Investigative), whereas type A (Realistic) appears the least predisposed. The correlation between personality types and awareness of respondents on environmental issues (Fig. 2) showed that Social type is the most sensitive to environmental issues. The type of personality of each respondent was associated, as it is deduced from his/her answers, with his/her personal beliefs, as they

are derived from his/her ranking of types: the internal consistency of the first type selected is 43%, whereas the internal consistency between the first and second choice is 81%. Each type's environmental question with the other questions in the group was also associated. The results gave R^2 values between 0.71-0.95, indicating medium to high correlation between the average values of scores of all other questions and the score of question that measures the environmental sensitivity.

The top-down correlation analysis, considering the ranking score of the respondents and the classification chosen by the respondent, gave the weighted rank correlations, r_T: (i) for the technical vocational school students, the range is between -0.053 and +0.707, with an average value of 0.355 and a standard deviation of 0.78; (ii) for the undergraduate students, the range is between +0.159 and +0.771, with an average value of 0.482 and a standard deviation of 0.218. Evidently, there is significant agreement between the two rankings for the six personality types, at least for the higher values of correlation. The hypothesis for the Pearson's, the Kendall's and the Spearman's correlation coefficients was formed. H_0: if r = 0, then there is no correlation; and H_1: if r > 0 or r < 0, then there is correlation. The confidence level is a = 5%. Thus, if *p*-value (two-tailed) < 0.05, then H_0 is rejected and H_1 is accepted; If r > 0, there is a positive

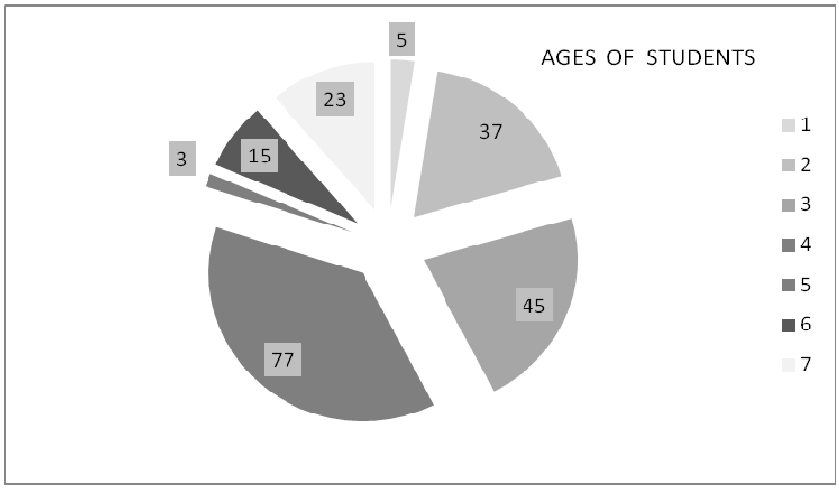

Fig. 1 Students' ages chart, where: 1 = 14; 2 = 15; 3 = 16; 4 = 17; 5 = 18; 6 = 22 and 7 = 24 years old.

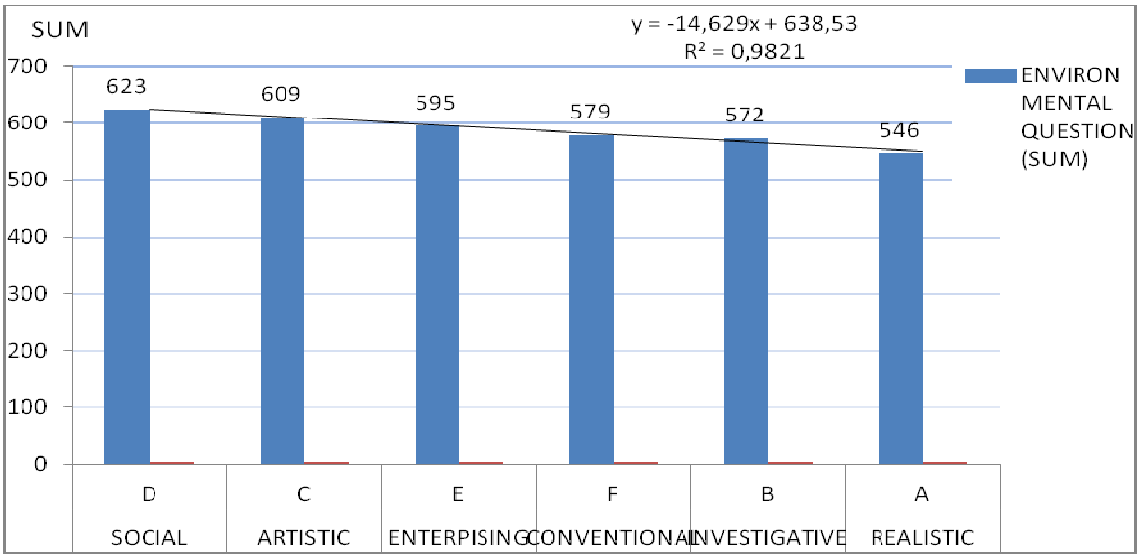

Fig. 2 Environmental question (SUM) of each type.

Table 1 Coefficients of correlation.

Holland's type	$r_{Pearson}$	$r_{Kendall}$	$r_{Spearman}$	Remarks
A	0.382	0.292	0.382	p (two-tailed) < 0.05
B	0.315	0.252	0.329	p (two-tailed) < 0.05
C	0.411	0.324	0.429	p (two-tailed) < 0.05
D	0.180	0.158	0.208	p (two-tailed) < 0.05
E	0.219	0.154	0.204	p (two-tailed) < 0.05
F	0.348	0.274	0.350	p (two-tailed) < 0.05

correlation whereas if $r < 0$, there is a negative correlation; in these cases, H_0 is accepted and H_1 is rejected. The results are presented in Table 1. As there is no linear relationship between variable "Initial Score" and "Final Score", the assumptions are based on Kendall' and Spearman' correlation coefficients.

4. Discussion

In Greek primary and secondary education, environmental education is included in the curriculum, yet it still depends on the educators' will to be applied. Administration bottlenecks, in addition to the uncertainty teachers are feeling concerning that their knowledge background on environmental issues, the lack of existence of a suitable educational or training material and the restriction of the school timetable usually hamper the environmental education course.

The theory of Holland's vocational personalities has been confirmed and validated by many researchers [6-10]. Using the modified questionnaire of personality types of Holland, without direct reference to them, this research has helped to elicit indirectly the views of students about the environment, so as to provide educators valuable information that they may use to formulate a proper educational material. Certain conclusions have been drawn at comparing personality types to environmental awareness, assigning a degree of environmental predisposition to each type.

Social is the first type of personality that is sensitive to environmental issues. The causal relationship that forms the Social type fully justifies this predisposition, as the main characteristics of the type are consistent with environmental sensitization: the Social type is friendly and responsible; he enjoys team work; he prefers educational activities; he cares for the public benefit and he tries to maximize social welfare. After all, the environment is a public good and its protection relies on willingness of the citizens.

The second type of personality that is sensitive to environmental issues is the Artistic one. This type develops positive feelings about the environment and is creative and unconventional. For this type, clean environment is a source of inspiration and creativity.

5. Conclusion

In conclusion, the modification of Holland's methodology for determining the degree of environmental awareness of young people has been proven suitable to evaluate attitudes and beliefs of students as regards their willingness to be actively engaged with the environment. The results obtained showed relative significant internal consistency at macro-level for almost half of the interviewees, but the dependence of answers to environmental queries on the rest responds to the rest queries was insignificant, indicating lack of specific knowledge and clarification of the corresponding concepts at micro-level.

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From the Iron Curtain to the European Green Belt Creating a Vision for a 2nd Transformation to a Life-Sustaining Europe/World

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Abstract: The European Green Belt developed from the wasteland of the former death strip along the iron curtain over decades to a green life line of biodiversity. It is an ecological network with a unique natural and cultural heritage, an emotional human and political history, meaning and transformative power. Due to the former border situation, it is a transnational green infrastructure with biodiversity hotspots in a more and more fragmented, intensively used and degraded European landscape and connects people from 24 European countries and valuable landscapes. But now, nearly 30 years after the peaceful transition in 1989, the gaps in the European Green Belt cover already 50%. These gaps are not protected and are subject to adverse effects, like ongoing landscape fragmentation and ongoing chemo-industrial agriculture. Alarming signals of a new death zone are not only the gaps within the European Green Belt, but generally and closely related the mass extinction of species, climate change, resource depletion, financial and economic crisis, demographic change, emigration, unemployment and/or precarious work worldwide. To save the European Green Belt and life on earth there is a great need of a 2nd transformation to a life-sustaining world.

Key words: European Green Belt, transformation, narratives, active hope.

1. Introduction

The European Green Belt and former Iron Curtain is a symbol for a gentle transformation: from death zone to life line, an unexpected change or peaceful transition. Some people call it even a miracle.

Now, 29 years after the historical fall of the Iron Curtain in 1989, this life line and ecological network full of biological diversity with a unique natural and cultural heritage, an emotional human and political history, meaning and transformative power [1] as seen in Fig. 1 is once again endangered. Moreover, 50% of this Green Belt through Europe are now unprotected gaps [2], a result of current policies, habits, priorities, related to a "business as usual" approach.

Signs of a newly arising death zone are not only the gaps within the Green Belt as presented in Fig. 2, but also closely related to the mass extinction of species, further climate change, resource depletion (peak soil, peak oil and peak everything), a worldwide destruction of ecosystems [3], financial and economic crisis, demographic change, emigration, unemployment and/or precarious work in Europe and worldwide.

This development highlights that now, 29 years later there is an urgent need of a 2nd transformation to maintain and restore the biological and cultural diversity to save life, including human life, god's creation.

2. Materials, Results and Discussion

In thankfulness to the development within the "GreenNet" project for the European Green Belt [2], working with project partners, scientists, people from the pilot regions, administrations, politicians and the transformations 2017 conference [4], there is now a 2nd transformation on the way!

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Fig. 1 European Green Belt: Pictures from top to down right: Graphic: © European Green Belt Initiative [5]. Aerial photo: The European Green Belt as a green infrastructure [6] within an intensive land use, © Klaus Leidorf [7], Embracing neighbours at the German border in 1989 after opening the wall in Moedlareuth, Germany, © Arndt Schaffner, Muenchberg [8].

It appears in form of a transformative science for sustainably living, a holistic science for example at the Schumacher's College in the UK [9].

The transformation is spreading up from the transition town movement [10], with head, heart and hand. The peace and alternative Nobel Prize winner Helena Norberg-Hodge shows in projects, books and movies, that local economy is the key to biological and cultural diversity and happiness [11].

Happiness is an important factor for human well-being. The Kingdom of Bhutan is a leading example of including it in economic accounting.

There is as well an urgent need to include natural capital with its ecosystem services in the economic accounting worldwide (TEEB: The Economics of Ecology and Biodiversity). Human kind depends on ecosystem services, the natural capital, for life, further decision making and real accounting for economy [12].

Fig. 2 Gaps within the Green Belt, mainly caused by still ongoing landscape fragmentation, for example by a new built autobahn, Germany © Marion Mueller [13] and still ongoing intensive chemo-industrial agriculture, Germany © Klaus Leidorf [14].

In 2009, the Nobel Prize for Economics was awarded to Elinor Ostrom with the topic of commons. Commons appear along the European Green Belt and general in forms of land sharing, food sharing, car sharing, repair cafes, urban gardening, social and ecological farming, local food, regional money, reskilling of crafts, intersectoral and transdisciplinary cooperation and in many forms more.

3. Conclusions

There are a lot of small signs of change, but to create a real impact it needs a strong vision, many people and a miracle like 29 years ago.

How to strengthen humans to contribute to transformation, change or miracles? Joana Macy and Chris Johnstone have developed a very relieving answer and book: "Active Hope How to Face the

Mess We're in without Going Crazy" [15].

The history and gentle transformation of the Iron Curtain/European Green Belt is a strong symbol, a ray of hope for the vision of creating a 2nd transformation to a life-sustaining Europe/world celebrating cultural and biological diversity and future.

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