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Kinetics of the thermal decomposition of pine needles

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Abstract: A kinetic study of the pyrolysis process of pine needles was examined using a thermogravimetric analyser. The weight loss was measured in nitrogen atmosphere at a purge flow rate of 100 ml/min. The samples were heated over a range of temperature of 19°C–600°C with a heating rate of 10°C/min. The results obtained from the thermal decomposition process indicate that there are three main stages: dehydration, active and passive pyrolysis. The kinetic parameters for the different samples, such as activation energy and pre-exponential factor, are obtained by the shrinking core model (reaction-controlled regime), the model-free, and the first-order model. Experimental results showed that the shrinking model is in good agreement and can be successfully used to understand degradation mechanism of loose biomass. The result obtained from the reaction-controlled regime represented actual values of kinetic parameters which are the same for the whole pyrolysis process; whereas the model-free method presented apparent values of kinetic parameters, as they are dependent on the unknown function $\phi(C)$, on the sum of the parameters of the physical processes, and on the chemical reactions that happen simultaneously during pyrolysis. Experimental results showed that values of kinetic constant from the first-order model and the SCM are in good agreement and can be successfully used to understand the behaviour of loose biomass (pine needles) in the presence of inert atmosphere. Using TGA results, the simulating pyrolysis can be done, with the help of computer software, to achieve a comprehensive detail of the devolatilization process of different types of biomasses.

Keywords: thermal decomposition, thermogravimetric analysis, kinetic models, pyrolysis, biomaterial, kinetic models

1. Introduction

The pines are coniferous, evergreen, resinous trees belonging to the genus *Pinus* of the family *Pinaceae,* native to the northern hemisphere. They are also found in South-East Asia and the Himalayan regions of India. The Chir pine (*Pinus roxburghii*) is predominant in the coniferous forests of the Himalayan regions of Uttarakhand and Himachal [1]. They constitute the major portion of the litter in coniferous forests [2].

Pine needles are abundantly found as underexploited biomass in coniferous forests and are responsible for forest fires and air pollution. According to the Forest Department of India, Dehradun, massive forest fires in 1995 engulfed 14.7 thousand acres of valuable forest area through 2,272 forest fire incidents in Uttarakhand, which created long-lasting ecological consequences [3]. Detrimental effects of fire make the top layer of the soil fallow and leave behind a layer of pine needles litter that prevents rain water from being absorbed by the soil, leading to the early depletion of the ground water cycle and stoppage grass growth, thus causing a scarcity of food for the livestock. Its tremendous potential as a combustible fuel for thermal as well as power application was studied through TGA (thermogravimetric analysis).

As forest residual logging, it would be wasteful to render the energy content of pine needles to a dump especially during times of increasing energy dependence. In addition, a higher level of utilization of pine needles would curtail ecological damages in hill conditions, and consequently, slow down the depletion of fossil fuel reserves. Using biomass as fuel instead of fossil fuel mitigates CO_2 emissions, as the evolved amount of CO_2 during the combustion process is compensated by the amount of CO_2 necessary for the photosynthesis process, hence it behaves as a CO_2 neutral source of energy [4,5]. Thermal and power generations are not only applications that biomass provides, but there are also several processes through which we utilize biomass for valuable products [6]. Biomass is a potential source for synthesizing the same chemical that is derived from crude oils. One of these processes is pyrolysis which belongs to the subgroups of thermo-chemical processes. In the pyrolysis process, the biomass decomposes into gases, liquid oils, and char. The information regarding pyrolysis and thermal analysis is studied in the papers of John E. White [7] and Paolo Ghetti [8]. Thermogravimetric analysis is often used for measuring mass losses and to know the mole fraction of evolved species during pyrolysis [9]. The main function of thermogravimetric analysis is online measurement of variations in mass as functions of time or temperature. Application of TGA is not confined to forestry or agricultural residual logging [10,11], but also for thermal decomposition of other materials such as medical waste [12], sewage sludge [13, 14], and waste car tyres [15]. Residues of biomass, mainly char, after devolatilization depend on the type of biomass used. The thermal

decomposition process is affected by operating parameters such as pressure, heat flow rate, temperature, and properties of biomass like moisture, bulk density, and composition. The bulk density of biomass influences the heat transfer into the particle and mass transfer from the particle. Hence, it is most significant to assure the best possible contact between particle and heating area [16, 17]. Various models regarding biomass decomposition are given, such as the isoconversional model that presumes kinetic parameters are inconstant during the process of decomposition but depend on conversion [18, 19]. Another model is the lumped kinetic model, which considers an ultimate number of parallel decomposition of n-th order reactions [20]. These partial reactions assist in complete decomposition run. As the pyrolysis process is the first thermo-chemical step in the gasification process, its chemical kinetics highly affect the yield of tar oil and char as well as their reactivity [21, 22].

Kinetic studies are very useful for the interpretation of reaction mechanism and catalytic phenomena, behaviour on molecular basis, optimization, and the development of new chemical processes as well as a gasifier design for bio-fuel extraction and simulation. In addition, the study of chemical reaction kinetics is of main interest to both chemists and the chemical engineering field. It can be used for elaborating rates data to attain various objectives [23]. The main significance of using kinetic analysis is to extract the valuable information on the pyrolysis steps through the different forms of kinetic models and their correlations. Eventually, it can be extrapolated to the industrial applications such as bio-fuel refineries. The pine forest tree is a resinous tree and easily catches fire. Its stability is maintained (or it does not decay) for many years due to the presence of a high percentage of lignin that provides strength to it. Therefore, we did a TGA analysis to know its thermal stability, its behaviour with inert gases, while the scope of using TGA results for simulating pyrolysis using computer software was to understand the devolatization of the different types of biomass.

2. Materials and methods

Pine needle samples for thermogravimetric analysis were taken from different altitude regions as: Dehradun (1,427 ft.), Teri Garhwal (5,740 ft.), and Champawat (5,280 ft.) districts in Uttarakhand. Pyrolysis of pine needles was performed using the thermogravimetric equipment, SDT Q600 (TA, Perkin Elmer etc) and Alumina (Al_2O_3) crucibles were used. A horizontal TG/DSC holder was used. Both DSC and TGC were performed to know the thermal as well as kinetics behaviour of loose biomasses. In order to achieve pyrolysis conditions, a nitrogen atmosphere was used. Nitrogen was used as the purge and protective gas protecting the micro-balance against possible pollutants. The volumetric discharge rate of nitrogen was set to 100 ml/min. for the purge gas. Thermogravimetric measurements were

carried out at a heating rate of 10°C/min. The furnace zone had to be purged for 60 minutes in order to drive off all the remaining oxygen. The mass of samples was measured between 12 and 21 mg. These measured samples are sufficient for a good contact area between the crucible and the sample. To measure the actual sample and furnace temperatures, thermocouple types R (Platinum-Rhodium-13%/ Platinum) were used.

The pine needles contained about 1.8 wt % of ash (on dry mass basis) during the pre-treatment of producer gas by heat exchanger and cyclone. The chemical analysis of pine needles was experimentally determined with the help of the CHNS-O analyser (Perkin Elmer 2400 Series), which is shown in *Table 1.*and *Table 2.*

Table 1. Proximate analysis and heating value of pine needle samples

Location (Samples)	Volatile Matter (%)	Ash content (%)	Moisture (%)	Fixed Carbon (%)	HHV*(MJ/kg)
Teri Garhwal	73.1	2.1	10.2	14.6	20.7
Rishikesh	68.4	2.1	11.6	17.9	20.8
Champawat	58.3	3.1	21.5	17.1	20.2

*High heating value (HHV) at constant volume

Table 2. Ultimate analysis of pine needle samples

Location (Samples)	C %	H %	O %	N %	S %
Teri Garhwal	54.05	5.34	32.58	0.56	0.19
Rishikesh	53.64	5.36	33.92	0.62	0.20
Champawat	53.36	5.91	31.77	0.61	0.17

Pyrolysis of pine needles

Various complex reactions are involved in biomass pyrolysis, which result in a large number of intermediates and products; hence, proposing an appropriate reaction mechanism and modelling the kinetic behaviour is extremely complicated. Nevertheless, it can be performed based on visible kinetics, which also urges researchers to propose a much more precise mechanism involving available experimental utilities. Usually, it is cumbersome to formulate an accurate mechanism which takes into account several experimental parameters and miscellaneous feedstock. All the mechanisms can be depicted by a simplified general method wherein our loose biomass as feedstock is transformed into

gaseous materials or volatiles, blackish tar, and char as the primary feedstock or end product for bio-refineries to transform it into bio fuels [24]. Solid char is formed in the temperature range of 200–400°C in the primary decomposition phase (however, it depends on the type of biomass one is using) and, consequently, it reacts at temperatures over 400°C, which is the second pyrolysis phase [25].

The main component of biomass is cellulose, which is often used as its model compound as of its simpler structure. An incipient mechanism of cellulose pyrolysis, the two-step competitive mechanism, shows cellulose transformation into volatiles in the first step and char evolution with gases in the second one was developed by Broido [26]. Antal and Varhegyi proposed to use the one-step reaction mechanism of the first-order reaction equation to show cellulose pyrolysis [27, 28]. Finally, it was concluded that complicated models including more than one reaction step are not necessary to be simulated with the rate-limiting step, the depolymerization of cellulose. Depolymerization can be clearly shown by the one-step mechanism of the first-order reaction equation with high activation energy [29]. However, this simplification seems inexact as the composition of light gases in pyrolytic mixtures [30, 31] proves that cellulose pyrolysis involves at least two reaction steps. These steps have to be competitive since the yield clearly depends on the heating rate. Although the postulation of two competitive reaction steps is not novel, it has been continuously modified and clarified [32]. The most important contribution has been done by bringing the so-called "active cellulose" or "intermediate" into the reaction chain [33, 34]. The multi-step lumped mechanism is shown in *Figure 1*.

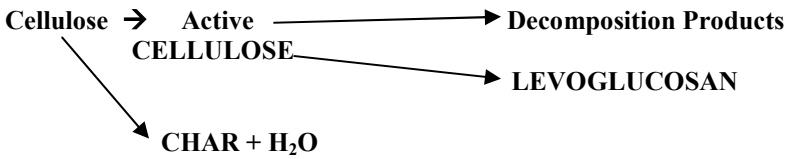


Figure1. Multi-step lumped mechanism of cellulose pyrolysis

The theory of kinetic modelling

Mainly, there are two types of methods used in kinetic modelling: model-free and shrinking core model (SCM, model-fitting method). The model-free approach implies that the estimation of kinetic parameters can be done without assuming a reaction model. Principally, there are two types of methods used in kinetic analysis: the so-called model-free and the model-fitting method. One of the methods is isoconversional, which usually uses model-free methods [35, 36]. According to the isoconversional principle, the reaction rate at a constant extent of conversion is a function of temperature only and the resulting kinetic parameters are dependent on

the conversion. The mostly used differential isoconvesional method is the Friedman method [37]. Model-fitting methods use a particular reaction model to obtain the best fit of experimental data resulting in the determination of kinetic parameters.

Each model-fitting algorithm implies minimization of the difference between the experimental and the calculated reaction rate values. A wide variety of reaction models is mentioned in the project of the ICTAC kinetics committee [38] together with appropriate model selection recommendations. Relating to an ICTAC kinetic study [39], reliability of the model-fitting methods is comparable with that of the model-free isoconversional methods if the fitting procedure is used simultaneously for multi-heating rates. The models used are discussed below.

Shrinking core model

The shrinking core model was first presented by Yagi and Kunii [40]. The various practical cases such as, fluid–solid reactions can be approximated as the first-order for mathematical simplicity [41]. This model should be employed for the first-order reactions and considers whether the rate of leaching process is controlled by the diffusion of the reactant or the rate of the surface chemical reaction. The heterogeneous leaching reaction can be shown as follows:

$$A_{fluid} + B_{solid} \rightarrow \text{Fluid product} + \text{Solid products}$$

The shrinking core model for an isothermal spherical particle is divided into three steps: diffusion of reactant A_{fluid} from the main body of gas film to the surface of the solid, reaction on the surface between reactant A_{fluid} and solid, diffusion of reaction products from the surface of the solid through the gas film back into the main body of the gas. A detailed integrated forms of kinetic laws (ϕ (C)) for different control regimes is detailed in *Table 3* [42].

In this model, the ash layer was absent and did not contribute to any resistance. Generally, the shrinking core model is used in the incineration process. The reaction mechanism, in the case of SCM, postulates that the reaction be carried out on the surface of a spherical solid particle [43]. The shrinking core model divided the control regimes into three parts what is shown in *Table 3*.

Table 3. Control regimes according to the shrinking core model (SCM)

Control regimes	ϕ (C)	k_s	Equation
Liquid film diffusion	$1-(1-\alpha)^{2/3}$	$2bDk_dC_A/\rho R_0^2$	1
Solid product diffusion	$1-3(1-\alpha)^{2/3}+2(1+\alpha)$	$2bDk_dC_A/\rho R_0$	2
Chemical reaction	$1-(1-\alpha)^{1/3}$	$2bDk_cC_A/\rho R_0^2$	3

Note: Where k_c means the apparent rate constant (reaction rate constant when the chemical reaction is rate controller for the shrinking core model, which depends on temperature and gaseous reagent concentration). We used equation (3) only in our kinetic analysis.

ϕ (C): Reaction model; b: Stoichiometric coefficient of reaction; D: diffusion coefficient in the porous product layer; C_A: Concentration of the leaching agent; ρ: Density of the solid particle; R_0: Radius of the unreacted particle; k_s: Reaction rate constant; α: conversion factor; k_d: reaction rate constant when diffusion is rate controller.

The kinetic parameters E (activation energy) and A (pre-exponential factor) can be obtained by using shrinking core model (SCM). If the integrated form of kinetic law i.e ϕ (C) = k_s is known, it can plot the values of ϕ (C) against time for different iso-thermal data points. Each of these plots should be linear, the slope being the value of apparent rate constant k_s at that temperature as the plot of ln (k) versus reciprocal temperature would be a straight line. The slope of straight line gives the value of –E/R, whereas intercepts provide ln(A). Regarding the SCM method, there is also an implicit assumption that the value of activation energy, E does not change during the course of reaction.

Based on the Arrhenius law for rate constant, rate constant can be expressed by the following equation

$$k = A \exp(-E/RT) \tag{4}$$

$$\ln(k) = \ln(A) - E/RT \tag{5}$$

The model-free method

The model-free differential isoconversional method was used to provide the apparent kinetic parameters. Integral approach fails to estimate activation energy E if the ϕ(C) is unknown [44]. Moreover, in SCM, it was assumed that evaluated E does not change during the reaction. On the contrary, in the model-free approach, the activation energy should be accepted as a variable parameter; therefore, E can be calculated at a different level of C. In general, the integral form of the rate equation is written as:

$$\phi(C) = k_v t \tag{6}$$

α = conversion or fractional mass remaining

$C = (m(t) - m_f)/(m_0 - m_f)$

$\alpha = (m_0 - m(t))/(m_0 - m_f)$

$1-\alpha = C$ (fractional mass loss)

$m(t)$ = instantaneous mass of sample

m_f = final mass of sample or residue mass

m_0 = initial mass of sample

k_v = rate constant for model-free method

$$\phi'(C)\, dC/dt = k \quad (7)$$

$$dC/dt = kv/\ \phi'(C) \quad (8)$$

$$dC/dt = kv\ F(C) \quad (9)$$

So, F(C) in the differential form of rate equation equals $1/\ \phi'(C)$. Invoke equation (5) and (9)

$$dC/dt = A \exp(-E/RT)\ F(C\ ) \quad (10)$$

Assuming a fixed value of C, equation (10) can be rewritten as follows:

$$\int_0^C \frac{dC}{F(C)} = A \exp(-E/RT) \int_0^c dt \quad (11)$$

$$1/(A \exp\left(-\frac{E}{RT}\right)) \int_0^c \frac{dC}{F(C)} = tc \quad (12)$$

$$\phi(c)/\ Ac \exp(-E/RT) = tc,i \quad (13)$$

$-\ln t_{c,i} = \ln (A_c/\ \phi(c)) - E_c/RT_i$

In the equation (13), i in subscript refers to isothermal condition $t_{c,i}$ is the time needed to reach a certain conversion isothermally, and A_c and $\phi(c)$ represent the pre-exponential factors and the integrated form of the reaction model. For the fixed value of C, it shows that a plot of the time against temperature in equation (13) would be a straight line; hence the value of -E/R will be obtained. So, E can be calculated at different levels of C.

Equation (6) can be modified in terms of temperature and conversion as follows:
if pyrolysis is carried out non-isothermally and temperature is the linear function of t (time), then:

$T = T_o + B\ t$

$B = dT/dt$ (°C/min)

B= linear heating rate

$(\frac{dm}{dt}) = k_c\ t$

$$-\int_{m_0-m_f}^{m_{(t)}-m_f} \frac{dm}{m} = \int_0^{t_c} k_v\ dt \quad (14)$$

For first-order reaction,

$$-\ln C = \int_0^{t_c} k_v\ dt \quad (15)$$

The right-hand side of the equation (15) can be modified by $k_v = A_C \exp(-E_C/RT)$

$$\ln C = -\ AC/B \int_{T_0}^{T} e^{-\frac{E_c}{RT}}\ dT \quad (16)$$

In 1961, Vallet, in a trilingual monograph, makes the substitution [45].

$z = -E_C/RT$

and reduces integral equation (16) to that for the expression

$\ln C\ = -\ (A_C\ E_c/R\ B) \int_z^\infty z^{-2}\ e^{-s} ds$

$J\ (z)\ = \int_z^\infty z^{-2}\ e^{-s} ds = z^{-2} e^{-s}\ S\ (z)$

$\ln C = -\ (\ A_C\ E_c/R\ B)\ J(z)$

Vallet evaluates the rapidly changing J (z) and the slowly varying S (z)(0.9564 to 0.9633) for range of z from $0 \leq z \leq 200$, thus covering various possible solutions for most problems.
In this way, we can obtain the value of ln (1-α) for a simple first-order reaction.
The order of reaction can be known by

$$-\ln\left(d\alpha/dt\right) = -n\ln(1-\alpha) + \ln(1/k) \qquad (17)$$

3. Results and discussion

Pyrolysis of pine needles

The thermal decomposition of pine needle samples is shown in *Figure* 2 (a–d). As it can be seen from the DTG curves, thermal degradation shows three peaks. The first one is up to about 55–67°C with a mass loss of about 1–1.5 %. The second one is in temperature interval of 300–305°C with 3 to 3.5% as mass loss, showing mostly the degradation of hemicelluloses. The third is found with mass loss of 5 to 5.5% at a temperature range of 340–350°C. Before the decomposition of pine needles started, some water and air moisture had got evolved. The end of drying is done at around 49 to 80°C. The process of biomass pyrolysis initiates above the upper limit of the given range, whereas, with wood, pyrolysis starts at 160°C [46]. The maximum mass loss of pine needles through pine needles decomposition cures (*Figure 2* (*a*) and *Figure 2* (*d*)) corresponding to temperature and time is obtained at around 345–350°C within 1800–1920 seconds. Temperature range was fixed below 600°C. The main decomposition regime (active pyrolysis) is in the range of 200–380°C approximately for three samples collected at different altitude levels with a mass loss of 56%. Above 387°C, an iota of mass (passive pyrolysis) undergoes final decomposition. Mainly hemicelluloses and cellulose in loose biomass (pine needles) decompose in the primal stage of active pyrolysis. In this experiment, decomposition rate reached two maximums at 305°C and 345°C, whereas lignin is decomposed in both stages. Passive pyrolysis which usually occurs at a very low decomposition rate, involves lignin decomposition. Although lignin degradation happens in the wide temperature interval of 160–600°C dichotomizing it from hemicellulose and cellulose decomposition is difficult. The peak complexity at higher heating rate usually occurs due to a relatively high content of hemicellulose degradation at lower temperatures as cellulose. It is obvious that carbon content in samples increase with temperature at the expense of decreasing fraction of hydrogen content in biomass. The pattern, which was experimentally found in *Figure 2* (*a–d*) clearly depicts that solid char is more charred due to the increasing temperature. In *Figure 2* (*b*), there can be seen a negligible increase in sample weight during experiment caused by the adsorption of gaseous reagents on

the solid surface, or the interaction of a very small fraction of CO_2 in the furnace with some components of a mineral layer (ash) of the char, which was observed during our studies of catalytic effects of ash in pyrolysis [47]. From *Figure 2* (*b*), the mass loss of samples begun at the temperature interval of 30 to 50°C and the maximum rate of change was observed at range of 300–400°C. The final residue obtained in the end was about 27 to 28% of the initial mass of samples. In an inert atmosphere like argon and nitrogen, the rate of decomposition is very slow and it decreases slowly. Such a process is ascribed to the gradual devolatilization of the char produced at lower temperatures [48] or it can be identified as corresponding to transformations of a part of the initial sample. Relating to kinetic modelling, such behaviour either refers to a reaction in series or to an independent parallel reaction. Unlike inert gases, in air, an increase in the rate of decomposition has been seen due to the oxidation of char, so that almost no residual mass is left in the end. Such behaviour was observed by Bilbao et al. [49].

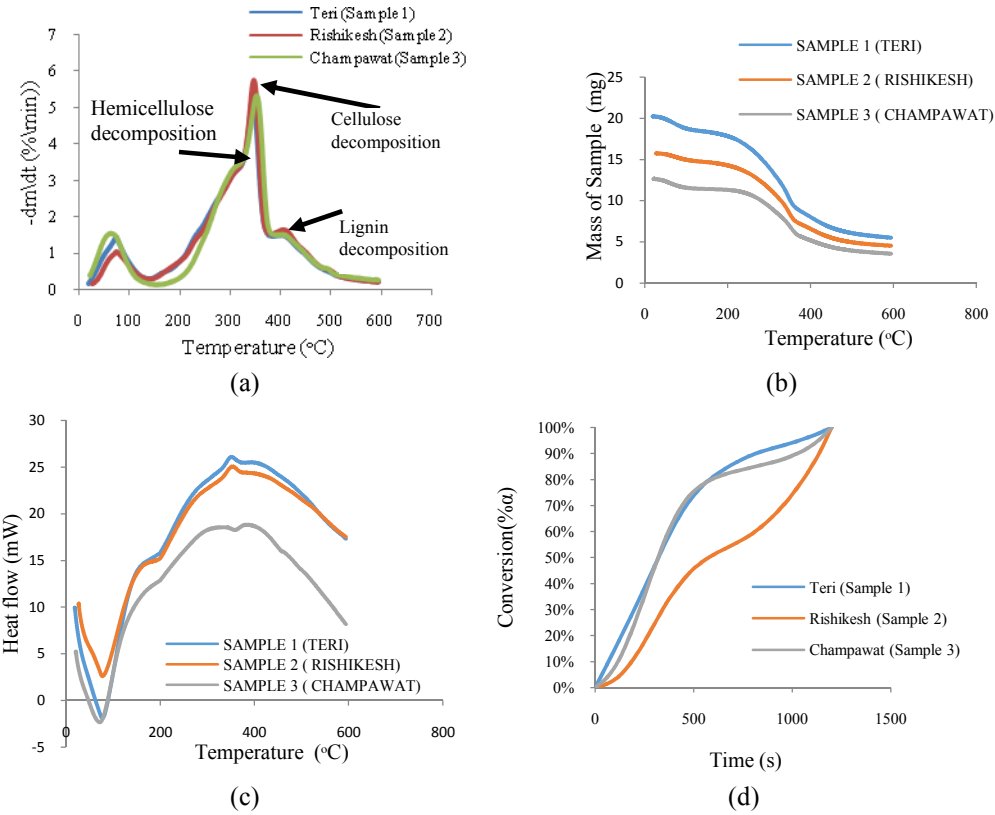


Figure 2 (a–d).Curves for the thermal decomposition of pine needles (TGA, DTG, and DSC) under inert atmosphere of nitrogen

Kinetics of thermal decomposition

Figure 3(*a–d*) shows the variation of fraction mass remaining of different samples with time and temperature. Supposing that pyrolysis is a first-order reaction, the calculation of kinetic parameters is done with the help of two methods: model-free iso-conversional and shrinking core model. In the kinetic modelling of biomass pyrolysis, a pseudo-homogenous kinetic equation can be involved [50]. Thus, the simple pseudo-homogenous reaction model for the first-order reaction with respect to pine needles as solid substrate can be used to predict the overall reaction rate. The reaction rate constants for the model-free as well as the shrinking core model are estimated from the experimental results as shown in Figure 3(a–d). The values of the slopes in plots provide reaction rate constants, which are represented in equation (6) and equation (3).

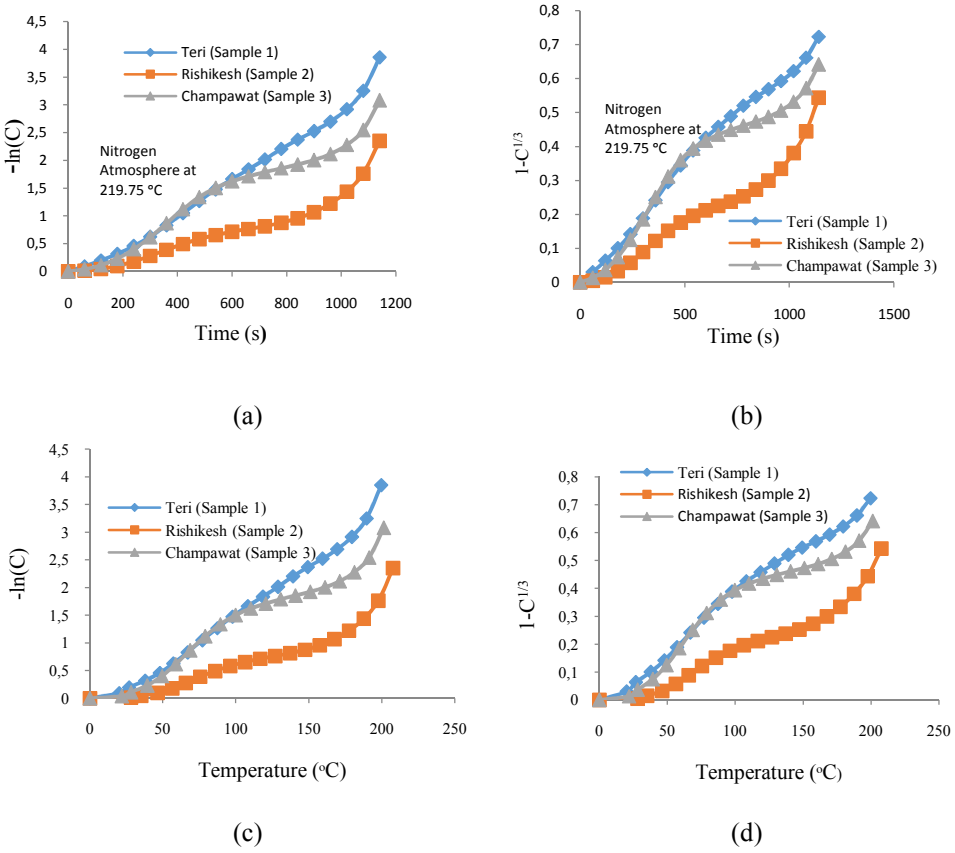


Figure 3 (a–d). Graphical plot of the linearized kinetic models (first-order model (a,d) and the shrinking core model (b,d)) for pine needles under inert atmospheres of N_2 with time and temperature

The relationship between the left-hand sides of equation (15) and equation (3), separately, must show the linear behaviour with time in order to prove the validity of first-order and shrinking core models. The role of these two equations in the experimental results obtained for the pyrolysis of pine needles can be seen in *Figure 3*. An experimental range of conversion varied from 5.7E-4 to 0.99 for all the three samples in an inert atmosphere. The curve fitting of data presented in *Figure 3* leads to the conclusion that the first-order reaction model can be applied only in the narrow range of conversion, whereas the shrinking core model relatively shows the good fitting of data points for the wide range of conversion. Having seen the curve fitting of data points, the validity of the first-order kinetics has likely indicated the pyrolysis of the pine needles proceeded, accordingly, to different mechanism. As it was seen in the results, the shrinking core models as well as the first-order model do not show a good agreement with the experimental data points at the higher rate of conversion. There is a likelihood that the limitation of diffusion can play a major role in this zone of conversion, which happened after 3300 s. The physical as well as chemical properties, residence time of volatile gases, heating rate and temperature are some major parameters that affect the pyrolysis of biomass. The pyrolysis of biomass at high temperature results in decreased char yield, mainly due to gasification reactions occurring at higher temperature [51]. As it can be seen from *Figure 3* (*b*), the shrinking core model in the regime of chemically controlled reaction is applicable up to a certain maximum value of conversion only. The higher volatile content in needle samples reduces the pyrolytic conversion rate as with the increasing temperature range of 370 to 592°C char yield decreases. The decomposition of cellulose in loose biomass gives higher bio-char yield at temperatures below 302°C. At temperatures above 302°C, cellulose depolymerizes, resulting high volatile content [52]. In the case of a high heating rate, the residence time has an insignificant effect on biochar yield, and hence suppresses dehydration reactions and the formation of less reactive anhydrocellulose, which provides a higher yield of char [53]. Thus, the effect of heating rate is stronger in the pyrolysis of biomass than that of other fossil fuels. Higher pyrolysis temperature also resulted in more liquid cracking, which provides a higher yield of gaseous products and a lower yield of tar and char [54].

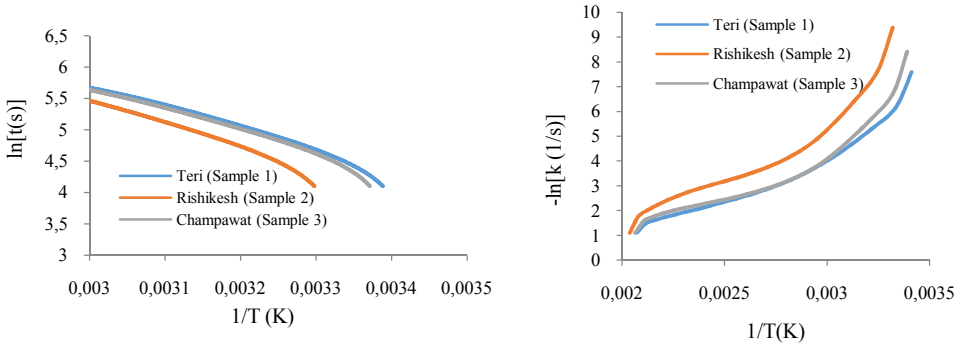
For all feedstock, large decreases in biochar yield were observed between the pyrolysis temperatures of 350°C and 500°C [55].

For the different volatile content, Sample 2 and Sample 3 have standard deviations of 0.01206 and 0.0120 respectively, whereas Sample 1 has the least standard deviation of 0.01 among the three samples.

Residence time at low temperature largely affects char yield rather than that of higher temperature. This is due to the fact that solid phase reactions are faster and therefore complete within 1 to 2 s. Secondary pyrolysis usually occurs at 700°C, but it has occurred earlier in the case of loose biomass, so the overall rate of

reaction decreased. During secondary pyrolysis, the rate of reaction which is the amount reacted in relation to the initial amount, decreases as the amount of substrate decreases [56]. The secondary reactions usually take place at around 700–800°C. These reactions occur mostly between the products of the primary reaction. The importance of secondary reaction increases with the residence time of volatile compounds in the hot zone of the reactor [57]. It can be concluded that high volatile and ash content reduce (first-order reaction) pyrolytic conversion rate at a higher temperature.

In *Figure 4* (*b*), at 335°C, all pyrolysis had taken place, and hence the slopes for all the samples went vertical to the abscissa and reaction rate abruptly increased with temperature, which led to fast pyrolysis reaction. In *Figure 2* (*c*), it can be also seen in DSC curves that there is a peak formation due to sudden increase in the heat of flow rate at the temperature range of 200–350°C. Relating to the variation in heat flow, Lee et al. [58] provided a view relating to the heat of reaction during pyrolysis. They estimated experimentally the heat of reaction through conversion rate, solid temperature and thermal properties, pyrolysis gas composition and pressures. It was found for an incident heat flux of 31.92 kJ/m^{2}s provided parallel to the grain direction, the pyrolytic region can be classified into three zones: an endothermic primary degradation occurs below 250°C, whereas an exothermic partial zone varies from 250°C < T < 340°C; and an endothermic surface char zone from 340°C < T < 520°C.



(a) (b)

Figure 4 (a–b). Arrhenius plots for pine needle pyrolysis in nitrogen atmosphere

Kinetic parameters obtained for the better-fitting models from the slope of straight line in *Figure 3* (*a–d*), are shown in *Table 4*. After correlating these values of rate constants with the temperature history (*Table 4*), the activation as well as the pre-exponential factors (*Figure 4*) were obtained. Using Equation 18, the order

of reaction (n) for pine needle samples was obtained, while thermal parameters obtained by DSC curves in *Figure 2* (*c*) are shown in *Table 5.*

Table 4. Kinetic parameters for pine needle pyrolysis in an inert atmosphere of nitrogen

Sample number	E (Activation energy) (kJ/mol)		A (Pre-exponential factor) (s^{-1})		Sample number	Temper-ature Range (°C)	$k_v(s^{-1})$ (firstorder model)	$k_s(s^{-1})$ (SCM)
Sample 1 (Teri)	SCM	Model-free	SCM	Model-free	Sample 1	300	4.53E-04	1.94E-04
	32.21	22.60	1274.105	1.08E-06		350	6.88E-04	2.42E-04
						400	8.63E-04	2.64E-04
						450	1.03E-03	2.79E-04
Sample 2 (Rishikesh)	40.55	23.64	6555.10	9.37E-07	Sample 2	300	3.26E-04	1.44E-04
						350	5.78E-04	2.43E-04
						400	7.74E-04	2.69E-04
						450	9.78E-04	2.86E-04
Sample 3 (Champawat)	34.52	22.61	2197.33	1.145E-06	Sample 3	300	3.93E-04	1.86E-04
						350	6.10E-04	2.30E-04
						400	8.43E-04	2.66E-04
						450	1.01E-03	2.80E-04

Table 5. Order of reaction and thermal parameters of samples (DSC curves) in an inert atmosphere

Sample Number	Order of reaction (n)	Specific heat (C_p)	ΔH (Net heat content)
Sample 1 (Teri)	0.32	22.5 kJ/kg K	0.262 kJ
Sample 2 (Rishikesh)	0.37	28.26 kJ/kg K	0.2181 kJ
Sample 3 (Champawat)	0.21	36.18 kJ/kg K	0.2256 kJ

The lower value of the parameter n (order of reaction) implies the strong inhibiting effects of nitrogen on the pyrolytic decomposition of loose biomass (pine needles). The activation energy and other parameters, especially by the shrinking core model, are in accordance with the earlier research experiment [59]. The lower value of the order of reaction in nitrogen was found to be the same by various methods that were discussed by Volvella et al. [60].

4. Conclusion and discussion

Needle samples obtained from the forest areas of Uttarakhand underwent a pyrolysis in a thermo-balance with an inert atmosphere of N_2 in order to study the thermal behaviour of loose biomass within the temperature range of 19 to 600°C at ramping rate of 10°C/min. The thermogravimetric experiments performed in a dynamic mode showed that the reactivity of pine needle samples was inhibited by nitrogen at a higher temperature. Moreover, decomposition rate with nitrogen was slower than that of the air or carbon dioxide, and transformation occured at very higher temperatures (>350°C). Most of the transformation occurs in a relatively narrow range of temperatures, which is different for each gas [61]. To understand the behaviour of loose biomass (pine needles), various models have been used to study the pyrolysis of biomass (viz. Two consecutive reaction schemes, Momentum equation for motion of pyrolysis gases, etc.). In this study, the simplest form of kinetics models for solid–gas reaction (the first-order model and the shrinking core model) has been implemented to find the better-fitting model for predicting the kinetic of chemical reaction during pyrolysis of loose biomass. The model-free method was only used to compare the values of activation energies and the pre-exponential function with the shrinking core model in order for a comprehensive study of the kinetics of loose biomass with other prevailing models. From all the results, it was concluded that the shrinking core model for the reaction-controlled regime predicted well for the rate of pyrolysis up to 95% conversion in nitrogen, whereas this was only 85% with the first-order reaction model. Activation energies (E) and the pre-exponential factors (A) were evaluated for both model-free and SCM. In addition, the order of reaction with respect to conversion rate was determined. In this kinetic study, the calculated kinetic parameters are within the range of values which were previously reported in the literature of the pyrolysis process of biomass [60].

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Effect of agricultural programmes on the livelihood of the vulnerable group: a case study of the Fadama III programme in Kwara State, Nigeria

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Abstract: This study examines the contribution of the Fadama III programme to the livelihood of the vulnerable group in Kwara State, Nigeria. Results revealed that the group was made up of mainly old, less-educated, small-scale farmers, with many years of farming experience. Benefits derived from the programme by the group include input support, asset acquisition, rural infrastructure, advisory services, capacity building, increased output, and income. The major constraints faced by the group were illiteracy, pests and diseases, inadequate inputs, and untimely funding. This study suggests policy measures on how to better the livelihood of the vulnerable group of farmers.

Keywords: contribution, benefits, constraints, measures

1. Introduction

With 173.6 million inhabitants, Nigeria is the most populous country in West Africa and constitutes 52.4% of West Africa's population [1]. Agriculture is the mainstay of the country's economy, accounting for about 40% of the gross domestic product (GDP) and providing employment to over 60% of the labour force and 90% in rural areas [2, 3]. Nigeria is blessed with good arable land, a friendly agricultural climate, a large consumer market – as indicated by the huge population –, as well as the ever-increasing world market for reaping the potentials

that agriculture can offer any economy [4]. Despite these plentiful agricultural potentials, Nigeria continues to experience widespread food insecurity and poverty, with 68% of the population living on less than $1.25 a day [5]. The vulnerable group is the worst hit in this regard [6].

One viable way of helping the vulnerable group is through interventions such as creating jobs or means of improving their livelihood [7]. Thus, in an attempt to improve the condition of the vulnerable group of its population, the Nigerian government most often includes this group of people in its agricultural intervention programmes. This group of individuals includes among others the disabled, the low-income group, the aged, unskilled population, isolated elderly people, widows, and orphans [3].

One of such agricultural-based intervention programmes is Fadama III. The programme is a tripartite intervention funded by the World Bank, the Federal Government of Nigeria, and participating States with objectives aimed at improving the livelihood of the beneficiaries (also known as Fadama User Groups – FUGs) in a sustainable manner. Though the primary focus of the project is targeted at involvement in food production, there is a tangential part involving social and economic support to vulnerable groups, such as widows, physically handicapped, the aged, and orphans, based on their identified needs.

Though many studies have focused on a generalized assessment of intervention programmes in Nigeria [8, 9, 10, 11, 12], none of them has paid specific attention to the vulnerable group as an important component of such programmes. This was the research gap which the study intended to fill. Knowledge about the clear picture of the assessment of the programme on vulnerable groups is desirable to provide agricultural policy makers an insight into the areas where the vulnerable groups require better assistance in order to improve their livelihood. In the light of this, the general objective of this study was to assess the influence of the Fadama III Development Programme on the livelihood of vulnerable crop farmers in Kwara State, Nigeria. The specific objectives were to:

1. examine the socio-economic characteristics of the vulnerable groups in the programme;
2. identify activities/services rendered by the programme to the vulnerable users;
3. determine the influence of the programme on the livelihood of vulnerable users;
4. identify the constraints confronting the group *vis-à-vis* their participation in the Fadama III programme.

2. Material and methods

Study area

The study was carried out in Kwara State, North Central Nigeria. The state is referred to as the "State of Harmony" and is one of the 36 states that make up the Federal Republic of Nigeria. It is located between latitude $8^0 5^l$ – 10^0 4^l N and longitude $4^0 55^l$ – $6^0 5^l$ E, covering an estimated land area of 36,825 square km with a population of about 2.37 million (NPC, 2006). The state was created in 1967 and is made up of 16 Local Government Areas (LGAs). It shares national boundaries with Niger, Oyo, Kogi, and Osun states and international boundaries with the Republic of Benin.

Kwara State is within the rain forest and the woody savannah areas. The state enjoys a tropical climate with an average rainfall ranging between 1,000 mm and 1,500 mm, lasting from eight to nine months of the year and a maximum temperature range of 30°C–35°C. It experiences two climatic seasons: dry and wet seasons. Agriculture is the main source of the state's economy.

The 16 LGAs in the state are grouped by the state's Agricultural Development Project (ADP) into four zones – A, B, C, and D – with their headquarters at Kaima, Patigi, Malete, and Igbaja respectively. The grouping was done in consonance with the ecological characteristics of the various parts of the state and for the effective administration of agricultural intervention programmes. The Fadama III programme covers all the four zones in the state. The beneficiaries of the programme were classified into groups otherwise called Fadama User Groups (FUGs) based on their enterprises.

Sampling procedure and sample size

The population for the study comprised vulnerable FUG crop farmers in Kwara State, Nigeria. Four-stage sampling technique was employed in the selection of respondents for this study. The first stage was a random selection of two (2) ADP zones from the four (4) ADP strata in the state. These were Zones C and D. The second stage involved a random selection of four (4) LGAs, two (2) from each selected ADP zone. These were Asa and Ilorin East LGAs in Zone C and Ifelodun and Irepodun LGAs in Zone D. Thirdly, with the assistance of the Fadama Community Facilitators, a list of vulnerable FUGs was compiled in each of the four LGAs, from which eight (8) vulnerable crop farmer FUG groups were randomly selected. Lastly, 185 vulnerable crop farmers were randomly selected from the eight FUGs based on the proportion of the vulnerable crop farmers in each group (*Table 1*).

Table 1. Sample design outlay for the study

Selected ADP Zone	LGAs	FUGs by communities	No of respondents
C	Asa	Alapa/Bakasse	21
		Lasoju	20
	Ilorin East	Agbayangi	21
		Iponrin	22
D	Ifelodun	Owa-Onire	24
		Idera	27
	Irepodun	Oro	24
		Ajase	26

Source: Authors' design

Sources of data and instrument for data collection

Data for the study were obtained from both primary and secondary sources. The primary data were collected with the use of interview schedule. Also, Focus Group Discussions (FGD) were conducted to make the study more interactive and participatory to determine the opinion of the groups about the context of the survey. Secondary data were also sourced from published and grey literature.

The instrument for data collection was structured questionnaire, the content of which was properly validated to ensure that the questions were relevant and without bias. The pre-testing of the instrument was carried out on 20 vulnerable FUG members in Bakasse (one of the FUG communities in Asa LGA of the state). The data collected include socio-economic characteristics of the respondents, services rendered by FADAMA III, benefits accrued from participating in the programmes, and constraints faced by the respondents vis-à-vis their participation in the programme.

Data analysis

Both descriptive statistics and Likert-type scale were used for this study. Descriptive statistics involving the use of frequencies, percentages were employed to analyse the socio-economic characteristics of the farmers and present the results of the findings. Likert-type scale was also used to assess the opinion of the farmers on how well the programme had improved their livelihood and the factors militating their ability to access the benefits of the programme. As regards the effects of the project on the farmers' livelihood, a five-point Likert scale was used and coded as follows: Strongly agree (5), Agree (4), Undecided (3), Disagree (2), and Strongly disagree (1). Also, a four-point Likert scale was used to assess the view of the farmers on the intensity of possible constraints facing the groups vis-à-

vis their participation in the programme. This was rated as Very severe (4), Severe (3), Less severe (2), and Not severe (1).

3. Results and discussion

Socio-economic characteristics of the respondents

The distribution of the respondents according to their socio-economic attributes is shown in *Table 2*. *Table 2* shows the socio-economic profile of the respondents. The majority of the respondents (41.1%) were in the 56–60 years of age-bracket. About 68.9% of the respondents were within the range of 61–75 years. The mean age of the respondents was 62.5 years. These results suggest that the group mostly consists of aged adults.

Also 68.1% of the respondents were male, while 31.9% were females. This indicates the dominance of male individuals in the group. The majority (76.8%) of the respondents were married, while just 0.5% was single. This suggests that crop farming is a means of catering for the family by the group.

Education is an important socio-economic factor as it determines the degree of innovativeness among farmers. About 35.7% of the respondents had no formal education, 22.7% attained primary education, and 15.7% attended secondary schools, while 3.2% and 1.6% had tertiary and adult education, respectively.

Household size is an important socio-economic variable as a large household size may determine the level of food security and poverty among farm households [11, 13]. The household size of the respondents ranged from 1 to 10 persons. The modal group is 4–6 persons, accounting for 59.5% of the respondents. Further analysis of the data revealed that the average household size of the respondents was about six persons.

Most (98.9%) of the respondents had been in farming for more than ten years. Also, the mean farming experience of the respondents was 13.2 years. This suggests that crop farming is an age-long venture for the respondents.

Regarding secondary occupation, 47.6% of the respondents had no other job except crop production, 30.8% engaged in trading, while 11.4% reported that they were artisans. This stresses the fact that crop production is a means of meeting the livelihood needs of this group of farmers.

Table 2. Distribution of respondents' personal characteristics (n = 185)

Variable	Category	Frequency	Percentage
Age (years) (Mean = 62.5years)	56–60	76	41.1
	61–65	64	34.6
	66–70	34	18.4
	71–75	11	5.9
Sex	Male	126	68.1
	Female	59	31.9
Marital status	Single	1	0.5
	Married	142	76.8
	Widow	37	20
	Separated	3	1.6
	Widower	2	1.1
Education	No formal	66	35.7
	Quranic	39	21.1
	Primary	42	22.7
	Secondary	29	15.7
	Tertiary	6	3.2
	Adult education	3	1.6
Household size	1–3	2	1.1
	4–6	110	59.5
	7–9	72	38.9
	≥10	1	0.5
Farming experience (years)	≤10	2	1.1
	11-15	7	3.8
	16–20	33	17.8
	21–25	36	19.5
	26–30	77	41.6
	> 30 years	30	16.2
Secondary occupation	None	88	47.6
	Trading	57	30.8
	Artisan	21	11.4
	Others	11	10.3
Contact with Fadama facilitator		185	100
Frequency of contact with facilitator	Regularly	137	74.1
	Occasionally	48	25.9
	Rarely	0	0
	Never	0	0
Farm size (hectares)	< 1.0	73	39.5
	1.1–2.0	86	46.5
	2.1–3.0	26	14
Source of farmland	Inheritance	169	91.4
	Lease/rent	5	2.7
	Purchase	11	5.9
Source of labour	Both family and hired	10	5.4
	Family labour	110	59.5
	Hired labour	65	35.1

Source: Authors' computation from field data

All the respondents had contact with Fadama facilitators, who served as extension agents between the farmers and the programme's co-ordinating office. However, 74.1% of the respondents had contact with facilitators on a regular basis, while the remaining 25.9% had this contact just occasionally.

About 46.5% of the respondents operated between 1 and 2 hectares, while 39.5% operated on less than 1 hectare of farmland. The average farm size of the respondents was 1.44 hectares. These results indicate that this group of farmers were mainly smallholders. Ninety per cent of the respondents acquired their farmland through inheritance, 2.7% through lease/rent, while 5.9% acquired theirs through purchase. The major source of labour to the farmers was family labour, and this served as a source of labour to 59.5% of the farmers.

Activities/services benefited from the Fadama III programme by the respondents

Table 3 shows the activities/services rendered by Fadama to vulnerable aged users. The *Table* shows that in terms of asset acquisition all the respondents had knapsack sprayer, wheel barrow, and protective wears. Forty per cent benefited from irrigation tools, 81.6% benefited from agro-processing facilities, while 38.9% and 2.2% benefited from storage facilities and power tilling equipment, respectively. Also, regarding rural infrastructure, the majority (73.5%) of the respondents benefited from potable water, 46.5% benefited from marketing facilities, but only 11.4% benefited from rural access roads.

Table 3 also indicates that all the respondents had access to input support, such as fertilizers, agrochemicals, and improved seeds, by virtue of participating in the programme. As regards advisory services, 98.4% of the respondents were trained on pest and disease control, 44.3% were trained on soil management, and 23.8% were trained on afforestation, while all the respondents were trained on sound agronomic practices. Regarding capacity building, 96.8% of the respondents were trained on how to resolve conflicts among users and non-users of the programme, 13% were trained on how to source market information, while all the respondents were trained on how to save and keep a proper record of their farming activities.

Table 3. Distribution of respondents according to activities/services benefited from the Fadama III programme (n = 185)

Category of benefit	Benefits derived	YES		NO	
		Freq.	%	Freq.	%
Asset acquisition	Storage facilities	72	38.9	113	61.1
	Irrigation facilities	74	40	111	60
	Agro-processing facility	151	81.6	34	18.4
	Knapsack sprayer	185	100	-	-
	Wheel barrow	185	100	-	-
	Protective wears	185	100	-	-
	Power tiller	4	2.2	181	978
Rural infrastructure	Marketing facilities	86	46.5	99	53.5
	Rural access road	21	11.4	164	88.6
	Potable water	136	73.5	49	26.5
Input support	Fertilizers	185	100	-	-
	Agrochemicals	185	100	-	-
	Improved seeds	185	100	-	-
Advisory services	Agronomic practices	185	100	-	-
	Soil management	82	44.3	103	55.7
	Afforestation	44	23.8	141	76.2
	Sustainable land management	2	1.1	183	98.9
	Pest and disease control	182	98.4	3	1.6
Capacity building	Conflict resolution	179	96.8	6	3.2
	Savings/record keeping	185	100	-	-
	Market information	24	13	161	87

Source: Authors' computation from field data

Influence of FADAMA III on the livelihood of the respondents

Table 4 shows farm production by the respondents before and after participating in the programme. The majority (57.8%) of the respondents cultivated between 0.6 and 1.0 ha of land for maize, 43.3% cultivated between 0.21 and 0.35 ha for cassava and 73% cultivated between 0.36 and 0.50 ha for yam. The output of most of the respondents were 1.1–1.5 tons/annum for maize, 2.1–4.1 tons/annum for cassava, and 3.1–4.5 tons/annum for yam, and this was obtained by 73.5%, 41.6%, and 73.0% of the respondents, respectively. The annual income of most of the respondents ranged from ₦51,000 to ₦100,000 for maize and cassava and from ₦101,000 to ₦150,000 for yam before the Fadama III intervention (Note: 1US$ = ₦165).

Tab. 4: Status of the respondents before and after the Fadama III intervention

Period	Crop	Farm size (Ha)	Freq.	%	Output (Tons)	Freq.	%	Total Amount (₦'000)	Freq.	%
Before Fadama III intervention	Maize	0.1 – 0.5	74	40	0.6 – 1.0	45	24.3	1 – 50	3	1.6
		0.6 – 1.0	107	57.8	1.1 – 1.5	136	73.5	51– 100	181	97.9
		1.1 – 1.5	4	2.2	1.6 – 2.0	4	2.2	101 – 150	1	0.5
	Cassava	0.06 – 0.20	77	41.6	0 – 2.0	65	23.2	1 – 50	3	1.6
		0.21 – 0.35	80	43.3	2.1 – 4.1	77	41.6	51 – 100	144	77.8
		0.36 – 0.50	28	15.1	4.2 – 6.2	43	35.2	101 – 150	38	20.6
	Yam	0.06 – 0.20	28	15.1	0.1 – 1.5	27	14.6	1 – 50	23	12.4
		0.21 – 0.35	22	11.9	1.6 – 3.0	23	12.4	51 – 100	40	21.6
		0.36 – 0.50	135	73	3.1 – 4.5	135	73.0	101- 150	122	66.0
After Fadama III intervention	Maize	0.1 – 1.0	5	2.7	1.0 – 2.0	4	2.2	10 – 100	5	2.7
		1.1 – 2.0	179	96.8	2.1 – 3.0	178	96.2	110 – 200	176	95.1
		2.1 – 3.0	1	0.5	3.1 – 4.0	3	1.6	210 – 300	4	2.2
	Cassava	0.1 – 0.5	43	23.3	0.1 – 4.5	43	23.3	1 – 100	3	1.6
		0.6 – 1.0	53	28.6	4.6 – 9.0	40	21.6	101 – 200	142	76.8
		1.1 – 1.5	89	48.1	9.1 – 13.5	102	55.1	201 – 300	40	21.6
	Yam	0.1 – 0.5	8	4.3	0 – 3.0	27	14.6	150 – 200	3	1.6
		0.6 – 1.0	26	14.1	3.1 – 6.1	32	17.3	201 – 250	5	2.7
		1.1 – 1.5	151	81.6	6.2 – 9.2	126	68.1	251 – 300	177	95.7

Source: Authors' computation from field data

After the Fadama III intervention, the majority (96.8%) of the farmers cultivated between 1.1 and 20 ha of maize farmland with an output of about 2.1–3.0 tons/annum (by 96.2% of the respondents) and an annual income ranging from ₦110,000 to ₦200,000 (by 95.1% of respondents). About 48.1% of the respondents cultivated between 1.1 and 1.5 ha farmland with an output of 9.1–13.5 tons/annum (by 55.1% of respondents) and an annual income ranging from ₦201,000 to ₦300,000 (by 76.8% of the respondents) for cassava production. Also, 81.6% of the respondents cultivated between 1.1 and 1.5 ha of yam with an output between 6.2 and 9.2 tons/annum (for 68.1% of the respondents) and an annual income ranging from ₦251,000 to ₦300,000 (for 95.7% of the respondents) (Note: 1US$ = ₦165).

Effects of the Fadama III programme on the livelihood of the respondents

Table 5 presents the distribution of respondents according to the perceived effects of the Fadama III project on their livelihoods. From the study, about 87.6% opined that their income increased through participation in the programme. The majority (84.3%) of the respondents strongly agreed that they were able to enrol their children in school. This, they claimed, was due to their increased income and improvement in socio-economic status. Meanwhile, 74.6% of the respondents claimed that they had enough food available in storage and about 66.5% strongly agreed that Fadama III was a source of employment opportunity to them. Also, over 70% of the respondents claimed increased social interaction within the FUG

group and 63.8% of the respondents agreed about having access to market information, which allowed them to sell produce beyond their localities. In the same vein, 86.5% agreed that their productive assets increased coupled with an improved standard of living through their participation in the programme. Likewise, the majority (81.6%) of the respondents opined that they were able to obtain assistance from government and other donor agencies by virtue of participating in the programme.

Table 5. Distribution of respondents according to the perceived effects of Fadama III on their livelihood (n = 185)

Benefit derived from FADAMA III	Strongly agree		Agree		Undecided		Disagree		Strongly disagree	
	Freq.	%	Freq.	%	Freq.	%	Freq.	%	Freq.	%
Increased income	162	87.6	23	14.4	-	-	-	-		
Enrolment of children in education	156	84.3	19	10.3	-	-	10	5.4	-	-
Increased food availability	138	25.4	47	74.6	-	-	-	-	-	-
Provide employment opportunity	123	66.5	62	33.5	-	-	-	-	-	-
Increased social interaction	47	25.4	130	70.3	-	-	8	4.3	-	-
Access to market information	-	-	118	63.8	2	1.1	56	35.1	-	-
Development of new technology	-	-	33	17.8	57	30.8	95	51.4	-	-
Increase of own productive assets	160	86.5	8	4.3	17	9.2	-	-	-	-
Assistance from community	17	9.2	16	8.6	86	46.5	66	35.7	-	-
Assistance from government/IDA	151	81.6	27	14.6	7	8.3	-	-	-	-

Source: Authors' computation from field data

Challenges faced by the respondents

The constraints limiting the respondents vis-à-vis their participation in the Fadama III programme are shown in *Table* 6. The foremost problem was the issue of pests and diseases, and this problem was faced by 85.9% of the respondents. This was followed by untimely release of funds with 87.6%, inadequate input (85.9%), limited income (73.5%), and illiteracy (65.9%).

Table 6. Distribution of respondents according to constraints faced by them in accessing Fadama benefits (n = 185)

Constraints	Strongly Severe		Severe		Less Severe		Not Severe	
	Freq.	%	Freq.	%	Freq.	%	Freq.	%
Limited land	36	19.5	18	9.7	107	57.8	24	13
Pest and diseases	159	85.9	18	9.7	8	4.3	0	0
Inadequate input	159	85.9	26	14.1	0	0	0	0
Untimely release of funds	162	87.6	23	12.4	0	0	0	0
Inadequate funding	144	77.8	41	22.2	0	0	0	0
Poor access to information	34	18.4	133	71.9	18	9.7	0	0
Non-accessible roads	0	0	103	55.7	59	31.9	23	12.4
Conflicts with herdsmen	12	6.5	117	63.2	53	28.6	3	1.6
Illiteracy	122	65.9	48	25.9	15	8.1	0	0
Limited income	136	73.5	47	25.4	2	1.1	0	0
Poor attitude of users	28	15.1	135	73	22	11.9	0	0
Due process policy	67	36.2	110	59.5	8	4.3	0	0
Incompetency of service providers	0	0	0	0	74	40	111	60

Source: Computation from field survey

Another important problem was the issue of conflicts between the farmers and herdsmen, about which 63.2% of the respondents agreed as being severe. Investigations during the survey revealed that the respondents' farmland was usually invaded by nomads in an attempt to source good pasture for cattle by the pastoralists. Poor access to information and non-accessible roads also posed severe problems to the activities of the farmers, with 71.9% and 55.7% of the respondents, respectively, agreeing about these constraints as being severe.

4. Conclusions

It can be inferred from this study that the Fadama III programme improved the livelihood of the vulnerable crop farmers in the study area. The study has been able to reveal an increase in farm size, farm output, income, and improvement in the livelihood of the vulnerable crop farmers after the Fadama III intervention. The programme also assisted the farmers in accessing input support, such as improved seeds, fertilizers, and agrochemicals, which enabled them to undertake farming operations as and when due. This group of farmers was also able to access new

technology in best production practices and increased social interaction with other Fadama users. The programme also generated employment and increased food availability for family consumption and income. It also encouraged this vulnerable group to participate in agricultural development. However, this group of farmers were constrained by many factors vis-à-vis their access to full benefits from the programme. These problems include illiteracy, pests and diseases, inadequate inputs, and untimely funding, among others.

Based on these findings, therefore, there is need for government and relevant stakeholders to provide this group of farmers with education. The facilitators of the programme (and of similar programmes aimed at assisting vulnerable groups of people) could also assist them through non-formal education. This could be through adult literacy programmes and extension education. This would help in solving the problem of illiteracy this group of farmers is facing. Also, efforts should be overhauled in providing the farmers with adequate inputs. Besides, the facilitators of the programme (and of similar ones) should strengthen their efforts in giving the farmers practical training on pest and disease management as well as soil management. Moreover, agencies responsible for releasing the fund for such programmes should always make it timely, especially to this group of farmers. This is not only due to their condition but also to the seasonal nature of crop farming.

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8-Hydroxyqunoline adsorption from aqueous solution using powdered orange peel: kinetic and isotherm study

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Abstract: Adsorption of 8-hydroxyquinoline (8HQ) on powdered orange peel (POP), a locally available adsorbent, has been studied. Experiment was performed on different 8HQ concentration, particle size, and adsorbent dosage. The Langmuir and Freundlich adsorption isotherm model has been tested. The obtained results best fitted the Langmuir model, suggesting monolayer adsorption of 8HQ on POP. The kinetic studies for the adsorption process were also carried out using pseudo-first- and pseudo-second-order models, and the data obtained is best fitted to the pseudo-second-order kinetic model. Thermodynamic parameters were calculated for the adsorption process and the result showed that the values of ΔG_{ads}, ΔH_{ads}, and ΔS_{ads} are -1171.4J/mol, -140J/mol and -40.5 J/K at 303 K. Thus, it can be summarized that the adsorption of 8HQ is spontaneous, chemisorbed, monolayer, and exothermic

Keywords: adsorption, 8-hydroxyquinoline, orange peel, isotherm model

1. Introduction

Water resources including fresh water are of great importance for natural ecosystems as well as human development, but they are becoming limited due to the increasing population, urbanization, and climate changes. This scarcity is basically due to water pollution, which is caused by the discharge of untreated or partially treated industrial effluents into the natural ecosystem, posing serious problems to it. Thus, these industrial effluents, containing a number of organic and inorganic chemicals, such as phenols, formaldehyde, 8-hydroxyquinoline, dyes, and heavy metals, are major water pollutants [1].

8-hydroxyquinoline is an organic compound with the formula C_9H_7NO. It is a derivative of the heterocycle quinoline by placement of an OH group on carbon number 8. This light yellow compound is widely used commercially, although under a variety of names [2, 3]. Heterocyclic aromatic hydrocarbons containing N, S, or O in the ring structure are one of the common contaminants of ground-water originating from coal gasification and oil refining processes, wood treatment processes, forest fires, automobile exhaust, and disposal of fuels and oils. Many of these compounds are reported to be toxic, carcinogenic, and they tend to accumulate in aquatic organisms even when present in low concentrations. Also the presence of the hetero atom makes them more soluble than their homo-cyclic analogues [4–7]. They are also used as preservatives in cosmetics and tobacco, chemical intermediates in dye synthesis as well as sophomoric and organometallic indicators, besides their wide usage [8].

8HQ and its derivatives should be removed from waste waters due to their toxic and harmful effects on aquatic organisms and human health. Several methods for treating organic pollutants from waste waters, such as precipitation, solvent extraction, or adsorption, can be used. Adsorption is one of the respective methods for waste water treatment due to its several advantages such as high efficiency, low-cost, simple application, and easy recovery of the adsorbent [9–11].

This work has been designed to remove 8HQ from aqueous solution through adsorption using orange peel powder as an adsorbent.

2. Material and method

The following chemicals were used for this study: hydrochloric acid, NaOH (BDH, England), and 8-hydroxyqunoline (98% sigma Aldrich) used for preparing the standard solution for the adsorption process. Orange peels were collected from Jimma town cafeterias to use as adsorbent material for the removal of 8 HQ from the aqueous solution. Distilled water and deionized water were used to prepare the standard stock solution. Analytical balance, Oven, Sieve (150μm), pH meter (pH211, HANNA), and UV-visible spectrophotometer (JENWAY 6705) were used in this work.

Adsorbent from orange peel

The adsorbent material, orange peel, was collected and washed with tap water followed by drying in the sun and chopping. The chopped orange peel is powdered and then washed with distilled water until its pH reaches 7 and is dried in the oven.

Preparation of the stock solution

0.1M of stock solution was prepared; by weight: 14.56 g of 8-HQ into 1L of hot water. Five standard solutions, (0.05M, 0.025M, 0.0125M, 0.00625M, and 0.00325M) were prepared by diluting hot water. 0.5 gm powdered orange peel was weighted and added into five shaking bottles, and followed by the addition of 25 ml (0.05M, 0.025M, 0.0125M, 0.00625M, and 0.00325M) in each of the five shaking bottles. Then the sample is shaken for 30 minutes and filtered using filter paper. The filtered sample is analysed by UV-Vis spectrophotometer at 325 nm.

Adsorption isotherm

In a solid–liquid system, adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (1): in this study, the extent of phenolic compounds adsorption capacity at equilibrium, q_e(μg/g), was calculated:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

$$q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

The percentage of phenolic compounds removal was calculated using Eq. (3):

$$(\%)Adsorption = \frac{C_o - C_e}{C_o} x100 \tag{3}$$

C_0 corresponds to the initial concentration of 8-HQ compounds and C_e(μg/g) corresponds to the concentration of phenolic compounds at equilibrium. V (L) is the volume of the solution and W (g) is the mass of the dry adsorbent.

3. Result and discussion

Calibration of 8-hydroxyquinoline

A calibration curve was composed of a minimum of a blank and three standards. A calibration curve was made for every hour of continuous sample analysis. More concentrated samples were diluted and the standard was falling on the plateau of a calibration curve – Fig. 1.

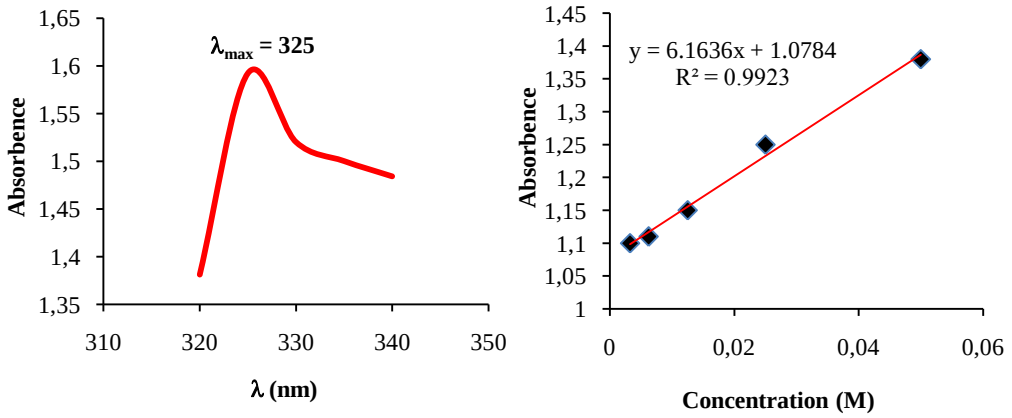

Figure 1. Calibration of 8-hydroxyquinoline in aqueous solution.

Adsorption isotherm study

Adsorption isotherm is a basic requirement for the design of an adsorption system. The adsorption mechanism was investigated using Langmuir and Freundlich models. The two models differ from each other in their assumption concerning the existence of fine adsorption capacity [12].

The Langmuir isotherm describes quantitatively the formation of monolayer on the outer surface of the adsorbent, and after that no further adsorption takes place – Fig. 2. The Langmuir isotherm is valid for monolayer adsorptions onto the surface containing a fine numbers of identical sites [13, 14].

The linear form of the Langmuir isotherm is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{C_e q_m b_L} + \frac{1}{q_m} \tag{4}$$

where q_e and q_{max} are equilibrium and maximum uptake capacity (mg/g), respectively; b_L is related to the free energy of adsorption and representing the Langmuir adsorption constant C_{eq} is the equilibrium adsorbate concentration in molarity.

The Langmuir constant which is related to the maximum capacity (q_{max}) and energy adsorption (b_l) can be calculated from the slope of linear plot $1/q_{eq}$ versus $1/C_{eq}$ as straight line.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L, which is given (*Table 1*) by

$$R_L = \frac{1}{1 + b_L C_O} \tag{5}$$

where b_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm to be irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1), or unfavourable (R_L>1). The value of R_L is found to be 0.897 mg/L at 303 K, indicating that the adsorption of phenol is favourable on the powdered orange peel.

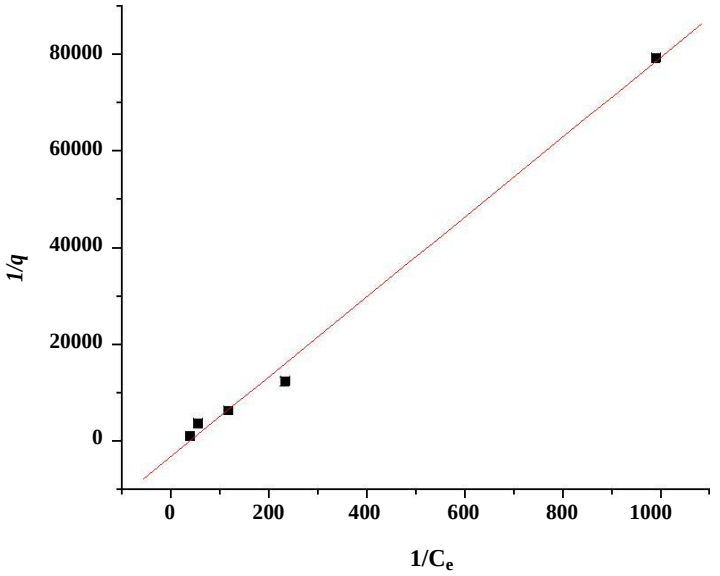

Figure 2.Isotherm model for the adsorption of the 8-hydroxyquinoline Langmuir model

The Freundlich adsorption isotherm is commonly used to describe the characteristic for the heterogamous surface. The linear form of the Freundlich is given in the following equation (Fig. 3).

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_f is an approximate indicator of adsorption capacity, while is function of the strength of adsorption in the sorption process and the smaller 1/n is the greater expected heterogeneity (d). n is lies between 1 to 10 this indicates a favourable adsorption process [15].

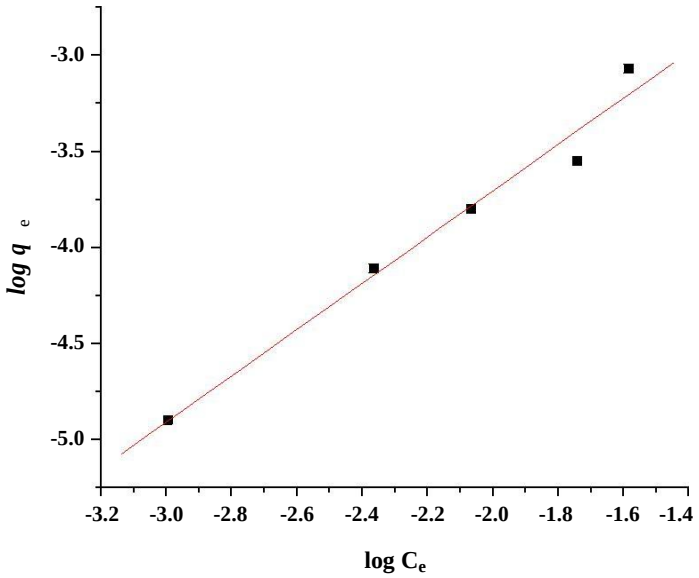

Figure 3. Isotherm model for the adsorption of the 8-hydroxyquinoline Freundlich model

From *Table 1*, the value of 1/n =1.2 and the value of R^2 is 0.988. Freundlich's model investigated adsorption capacity K_f and adsorption capacity (1/n). K_f intercept is 0.05mg/g, showing appreciable affinity for the 8-hydroxyquinoline adsorption; the value of n ranging from 1 to 10 shows a favourable adsorption. The correlation coefficient value is 0.988 and it shows that the Freundlich model is not applicable to equilibrium as compared to linear Langmuir models (R^2 = 0.997), which indicate monolayer formation on the surface of the adsorbent.

Table 1. Isotherm parameters for 8-hydroxyquinoline adsorption on orange peel adsorbent

Adsorption isotherm & constants	**Values**
Langmuir	
q_m (mg/g)	0.012
b_L(L.mg^{-1})	-0.027
R^2	0.997
R_L(mg/L)	0.897
Freundlich	
1/n	1.205
K_f	0.051
R^2	0.988

Adsorption kinetics

Adsorption kinetics is significant in evaluating the performance of a given adsorbent and in getting an insight into the rate of adsorption and the rate-limiting step of the transport mechanism, which is primarily used in the modelling and design of the adsorption process. In order to evaluate the kinetics parameters, pseudo-first-order and pseudo-second-order equations were implemented to analyse the experimental data. The pseudo-first-order equation can expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{7}$$

where q_e and q_t are the amount of adsorbate in mg at equilibrium at any time t, while k_1 is the first-order rate constant (min^{-1}).

From the plot of Log ($q_e - q_t$) versus t, in *Figure 4*, k_1 can be calculated from the slope and theoretical q_e can be obtained from the intercept.

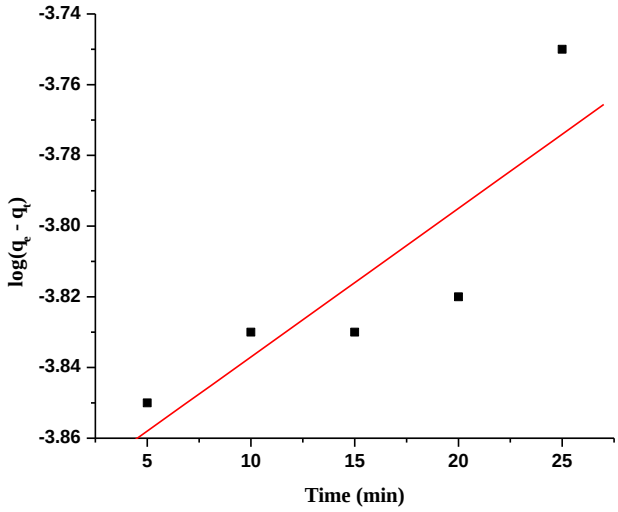

Figure 4. Pseudo-first-order kinetic model for 8-hydroxyquinoline adsorption on powdered orange peel

The pseudo-second-order equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

where k_2 is rate constant of second-order adsorption. The linear plot of $\frac{t}{q_t}$ versus time gives $\frac{1}{q_e}$ as slope and $\frac{1}{k_2 q_e^2}$ as intercept – *Fig.5*.

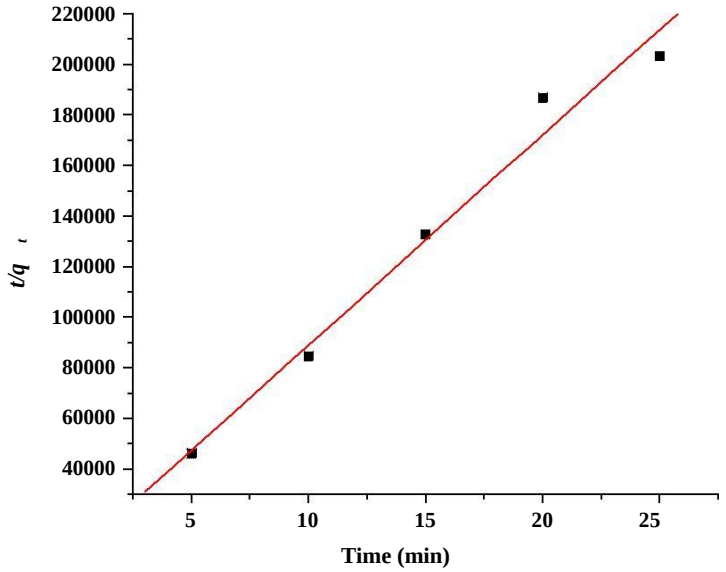

Fig. 5. Pseudo-second-order kinetic model for 8-hydroxyquinoline adsorption on powdered orange peel

The adsorption of 8-HQ onto orange peel shows a rapid initial adsorption rate followed by a slower rate. Initially, adsorption sites are abundantly available and 8HQ interacts easily; hence, a higher rate of adsorption was observed. However, after the initial periods, the lower adsorption may be due to the slower diffusion of adsorbate into the interior adsorbent. The two adsorption kinetics models mentioned above have been used to understand the adsorption kinematics and correlation coefficient, R^2, where calculated from plots. The linearity of those plots indicates the capacity of the two models. The correlation coefficient adsorption kinematics is 0.863 and 0.990 for pseudo-first-order and second-order, respectively. The correlation coefficient shows that the pseudo-second-order models fit better to the experimental data than the pseudo-first-order models. The obtained constants for the pseudo-first- and pseudo-second-order kinetics model are tabulated in *Table 2*.

Tab. 2. Kinetics parameters for the adsorption of 8-hydroxyquiniline from aqueous solution

Kinetic models &constants	Values
Pseudo-first-order	
$q_e$cal.(mg/g)	1.32E-04
$k_1(min^{-1})$	0.0096
R^2	0.863
Pseudo-second-order	
qecal. (mg/g)	1.20E-04
k_2(L/mg.min)	11,607.08
R^2	0.990

Adsorption thermodynamics

In order to fully understand the nature of adsorption, the thermodynamics parameters such as the standard Gibbs free energy, the standard entropy, or the standard change in enthalpy can be calculated using the following equation:

$$\Delta G^O = -RT \ln K_c \tag{9}$$

where the gas constant (8.3145J/mol.K) is the absolute temperature in Kelvin and K_c is the standard thermodynamic equilibrium constant defined by C_o/C_e, and the temperature change from 303 to 313K was computed from the following equation:

$$\ln K_c = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{RT} \tag{10}$$

ΔH (kJ/mol) and ΔS (kJ/mol) were calculated from the slope and the intercept of linear plot of $\ln K_c$ vs 1/T. Enthalpy change (ΔH) is used to identify whether the adsorption process is exothermic or endothermic, but the standard entropy change determines the disorders of adsorption at solid-liquid interface [16]. The thermodynamic parameters of adsorption where calculated using equations (9) and (10); the calculated value of these parameters are given in *Table 3*.

Table 3. Thermodynamic parameters for the adsorption of 8-hydroxyquiniline from aqueous solution

T (K)	lnKc	ΔG_{ads}(J/mol)	ΔH_{ads}(J/mol)	ΔS_{ads}(J/mol)
303	0.465	-1171.4		
308	0.444	-1136.9	-140	-40.485
313	0.339	-882.2		

The negative values of enthalpy confirm that the exothermic nature of the adsorptions process and -140 (J/mol) amount of heat is released during the binding

of 8-hydroxyquiniline on the surface of orange peel. The negative value of entropy indicates decreasing randomness at solid-liquid interface during adsorption. The negative values of ΔG confirm that the adsorption process is spontaneous, which becomes a less negative value with an increasing temperature, indicating that adsorption occurred at a lower temperature.

4. Conclusion

8HQ can be removed effectively on powdered orange peel. Batch adsorption was applied and the result revealed that the equilibrium adsorption was attained at 30 minutes. The adsorption isotherm can be well described with the Langmuir model within the studied conditions. Results of kinetics study indicate that the pseudo-second-order kinetics can simulate the adsorption process with a high accuracy for the adsorption of 8HQ from aqueous solution. Thermodynamic parameters for adsorption, such as ΔH^o, ΔS^o, and ΔG^o, were calculated for the adsorption process, and the result showed that the free energy, enthalpy, and entropy of adsorption were -1171.4 J/mol, -140 J/mol, and -40.485 J/mol at 303 K, respectively. This indicates that the adsorptions of 8HQ are spontaneous, chemisorbed, mono-layered, and exothermic.

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Sustainable revitalization of brownfield lands – possibilities of interim utilization in the form of urban community gardens

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Abstract: Our PhD researches include brownfield revitalization,[1] the application of the methods of interim utilizations on greeneries,[2] and the formation background and potential of community gardens.[3] We compared our systems of criteria in hope of extensive research conclusions. In order to trace the urban development possibilities in Budapest, we analysed brownfield revitalizations where the interim utilizations included allotment gardens, too. We concluded that such developments are likely to create environmental and social added value. Early results of the valorization process are important by themselves, but the perpetuation of interim land utilization holds even greater values.

Keywords: brownfield, revitalization, interim utilization, urban allotment garden, landscape architecture

1. Introduction

The main aspect of the *successful* urban development and land use of today and the near future is *sustainability* and *reclamation*. This tendency can – and has

[1]Adorján, A. Urban development aspects of the revitalisation of brownfields, ecological, economical and social sustainability
[2]Sipos, A. Temporary and transitional utilization of unused areas from a landscape architecture point of view.
[3]Fáczányi, Zs. Present and future of community gardens in Budapest.

to – be followed in land use by revitalizing "brown belts," brownfield areas, and former industrial areas.

Reclamation

Brownfield sites present great development opportunities for cities as reclamation of sites; however, their revitalization meets significant difficulties. We use the term 'brownfield' as it is accepted in the Hungarian terminology:

"A brownfield is a less efficiently utilized (underused), sometimes exhausted ex-industrial area. But the badly utilized or abandoned railway and emptied military territories can be considered brownfields as well." [1]

After the successful transition, these areas and their open spaces can once again become an organic part of the cultural and economic life of the city, the local identity, and the green surface system as well.

Success

We consider successful those brownfield renewal projects which have a positive effect on the users of the territory from an economic, social, and environmental point of view.

Brownfield redevelopment projects and especially its open spaces are in a serious disadvantage in comparison with greenfield developments since during their earlier utilization they were affected by different human activities which might call for a significant amount of damage control. Environmental decontamination and the elimination of hazards might account for 50–70% of the total budget, and this only results in a completely neutral, harmless area with no specific values of its own. This is why the reuse of such territories and the rehabilitation of its open spaces is an even greater achievement.

Due to the differences between the sites, the diversity of goals and available tools, it is difficult to formulate guidelines for their reuse that could be applied anywhere in order to be 'successful'. Among the wide range of tools, there is the interim and temporary utilization, which may contribute to the success of the renewal of an area [2 b].

The key to a successful redevelopment is also the renewal of the image of the property, which can either be done quickly, and with large investments or by more subtle means but in a longer time period. Our opinion is that after the economic crisis the urban development needs a new approach in which the slower and more community-based renewals get a bigger role. Interim utilization is a part of that, and these can provide opportunities for community involvement and development as well.

Sustainability

"Europe needs cities and regions which are strong and good to live in.", states the Leipzig Charter on Sustainable European Cities, which was presented at the time of the German presidency of the Council of the European Union, in May 2007, at the informal meeting of the ministers. The Charter emphasizes the fact that local governments should pay special attention to the cities' efficiency, to the quality of the built environment, and to sustainability.

The sustainable redevelopment in the cases of brownfields or any other underused areas means land utilizations which improve the city from an ecological point of view, but its creation, maintenance, and operation do not burden the economy. In the case of open spaces, the degree of utilization of the property depends on the community forming capabilities of the functions and on a longer term on the presence of a layer with an adequate system of preferences.

The interim utilizations, and within those the functions of the allotment gardens, meet these criteria. In this article, we look at the roles of interim utilization and allotment gardens in the successful and sustainable revitalization of brownfields.

2. Materials and methods

We look at the methods of interim utilizations implemented within brownfield revitalizations, interpret the completed allotment gardens, and try to compose further research topics through relevant examples. Our aim is to compare our research areas in order to make further progress in our researches and to draw our own conclusions as well.

Interim utilization

The interim utilization presents temporary and quick solutions to the changed needs of the urban dwellers, adapting in the same time to the tough economic situation. This new form of planning and design gives alternative answers to the current questions of urban planning, bridging the difficult investment periods.

The interim utilization can be achieved in urban areas that are unused and can be occupied for a particular period of time and a particular purpose. This idea has become really topical by today for there have been more and more unused, mainly industrial and railway, areas since the end of the 20th century. Budapest is a real treasure chest from this point of view.

The tools of interim utilization help bridging the functional gaps found in the prolonged transformation of a city area. With their help, new and on-site happenings can be triggered, which are essential for the revival of the area. In order

to be successful, we need a functioning concept realized on the property, which can maintain interest for a sufficiently long period of time and which can create constant intense connection between the community and the site. Not only it creates a unique atmosphere, but it also gives time for the area to be incorporated into our own identity and can positively influence its perception. Although these utilizations are mostly temporary in the urban environment, they help the planning based on public participation and urge people to be more responsible for the shaping of their surroundings [3].

Definitions

According to the Hungarian terminology: "Interim utilization means the temporary utilization under special conditions of territories and inner areas which are in transition between abandonment and future utilization." [4]

"Interim utilization falls between the original utilization of a particular territory (industrial, military, religious, etc.) and a new intended, in most of the cases yet to be determined use. Thus the interim utilization cannot be fully defined neither from the point of view of the activity or the time period of the utilization, nor from a legal perspective." [4]

For the sake of interpretability of interim utilization, we introduced more new notions. So, henceforward, within interim utilization, we are going to differentiate between temporary and transitional utilization.

In our interpretation, the interim utilization refers to the use of an area which – after a not yet foreseeable period of time – will be followed by another type of utilization, typically a greater investment. The location of the interim utilization is usually an abandoned area and because of temporality the architectural design is characterized by specific materials.

Temporary utilization is a form of interim utilization when a territory is used for a shorter period of time regardless of its past or future. Temporary usage usually means point-like events and in most of the cases the architectural and programme elements are terminated completely after the end of the utilization; they are changed and not used at all for the subsequent investments.

Transitional utilization is a type of interim utilization in which the present usage of the area is trying to make contact with the future and maybe the past usage as well. The significance of this utilization lays in the fact that it brings the area into the public consciousness before the future investment, and prepares its greeneries for a later use. Transitional uses generally have an overall programme and because of its continuity some of its elements can span into the stages after the bigger investments [3].

Examples

I would like to illustrate the interim utilization through two projects, one of which has already been completed and the other one is yet to be implemented. In both cases, the brownfields (the airport of Berlin and spare territories of Nyugati Railway Station in Budapest) present an ideal area for the complex projects that include allotment gardens and recreational open spaces.

Berlin, Tempelhof

The interim utilization is at its peak in Germany and especially in Berlin. The number of completed projects is high, but their role within the city and their quality is even higher. The Tempelhof, the unused airport of Berlin, is an exemplary project of the city.

The interesting part of it is that the co-operation was so successful and the community's needs were fulfilled to such an extent that when the interim utilization ended civil protests began to continue the project. Eventually, the city administration gave in and approved the established functions to be permanent; thus, the highly used large allotment gardens on the site continued to function as well. It is very likely that the allotment gardens played an important role in the life of the community, who managed to keep the territory for themselves even against the powerful market players.

Figure 1. Berlin,Tempelhof

Budapest, Nyugati Grund

The interim utilization in Budapest is at its early stages; more complex projects only exist on the drawing table. There is a project devised for the 2-ha unused property of Nyugati Railway Station, which has become known as the Nyugati Grund.

This plan covers a span of eight years and is broken down to six stages. One of the most important elements of the design is the allotment gardens, which could generate a new community, thus creating new owners for the Grund.

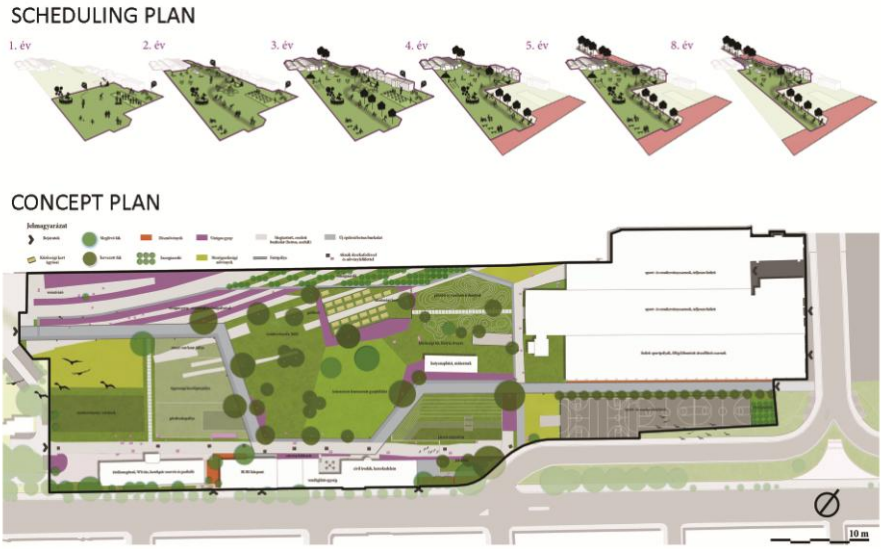

Figure 2. Scheduling plan; Concept plan: Andrea Sipos: The temporary utilization of the Nyugati Grund

Community gardens

According to the summary of the American Community Garden Association, a community garden can simply be seen as "any piece of land gardened by a group of people" [5]. There is a wide scale of different forms of urban agriculture such as the allotment and worker's gardens of the 19th century in Europe, the war- and crisis gardens during the World Wars, or the subsistence farming of the "reborn" urban food production in Cuba at the end of the 1980s – besides the creative urban farming projects of the last decade. Actions of guerrilla-gardeners and the opening of the Bowery Houston Farm, as the first community garden in New York in the 1970s, were milestones on the way of citizen engagement in the creation of new public spaces, focusing on the generation of communities and reuse of vacant plots [6].

Definitions

To formulate the relevant characteristic of community gardens, we can use Christina Liesegang's definition: "community gardens as public or semi-public green spaces create certain urban or place qualities for the neighbourhood and for

the city in general. Most of the time, empty, abandoned land is used and upgraded and community spaces as well as access to urban nature are created" [7]. As she outlines, most of the cities have problems with the maintenance of public spaces because of decreasing financial resources and the insufficient presence and quality of neighbourhood communities. "Community gardens bring a different type of green spaces into the city. They contribute to the overall diversity, not only in the sense of enhancing the variety of plant and animal species, but also by, for example, enriching leisure possibilities of the inhabitants of urbanized areas. They are small-scale, low-tech and bottom-up initiatives that may have the potential to make a change on a much wider scale than in the area of their own." [8]

Examples

Berlin, Prinzessinengärten

Prinzessinengärten (Princess Gardens) is an example for the generated excellent urban quality at a pilot project started in the summer of 2009 at Moritzplatz in Berlin Kreuzberg, a site which had been a wasteland for over half a century. Along with friends, activists, and neighbours, the group cleared away rubbish, built transportable organic vegetable plots, and reaped the first fruits of their labour [9].

Figure 3. Berlin, Prinzessinengärten before and after

Budapest, KerthatárKert community garden

"KerthatárKert" community garden was founded by the Contemporary Architectural Centre (KÉK)[4] at the south of Pest, getting the firm-owned, unused, partially concrete-covered territory. Participants of the neighbourhood intend to grow vegetables and also develop an educational area on one hundred parcels, each of them being 8 square meters.

[4]The "Contemporary Architectural Centre" (KÉK) [10] and the "Urban Gardening Association" (VKE) [11] are the very active groups in the organization of community gardens in Budapest.

Figure 4. KerthatárKert community garden

3. Results

The land requirements of allotment gardens can vary. The garden communities in Budapest usually prepare 25–80 individual seedbeds and create a common spice garden, a resting area on a 700–1000-m^2 plot. As brownfield developments are of a larger scale and mostly involve buildings that need rehabilitation, it would be interesting to implement further urban agricultural functions, such as aquaponic farming, seedling growing, and in-door farms using artificial lights. The more and more fashionable agricultural park could be adequate as well combining several functions of open space land use.

The production in the urban allotment gardens is usually irrespective of the soil; raised or mobile seedbeds are the most common. Thus, should the interim utilization be replaced by a real estate development, the garden can be relocated and it can be used with as much efficiency on brownfields as well since it is not affected by soil pollution. In such cases, gardening makes possible the simultaneous use of sites, and in the case of brownfields the rehabilitation of the potentially contaminated soil is also possible with the method of phytoremediation.

Analysing the position of community gardens in Budapest, we can draw conclusions on the conditions of their formation. Based on currently existing comparisons, the most telltale aspect is the correspondence between the position of the gardens and the type of residential area, which unequivocally shows that the presence of downtown gardens in numbers is significantly small, while the number of gardens around housing estates is much higher (Fig. 5. Budapest – dwelling areas according to the way of building-in) [6].

The delineation of urban community gardens' potentially contaminated soil, to revitalize the brownfields, may lead to further areas of development; the mobile or lifted planting beds, widely used in urban gardens, could be sustainable

alternatives for the conversion of such territories to green by plantation (Fig. 6. Budapest – soil contamination in brownfield areas).

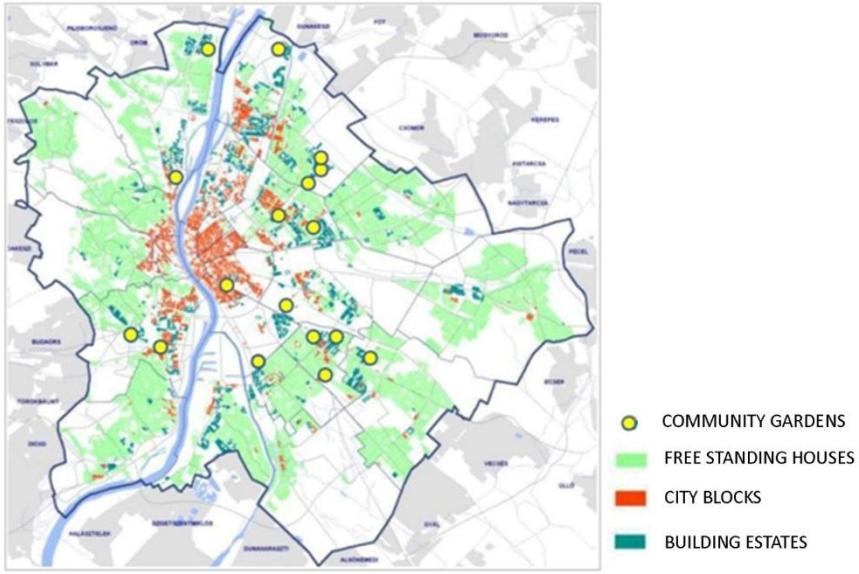

Figure 5. Budapest – dwelling areas according to the way of building-in

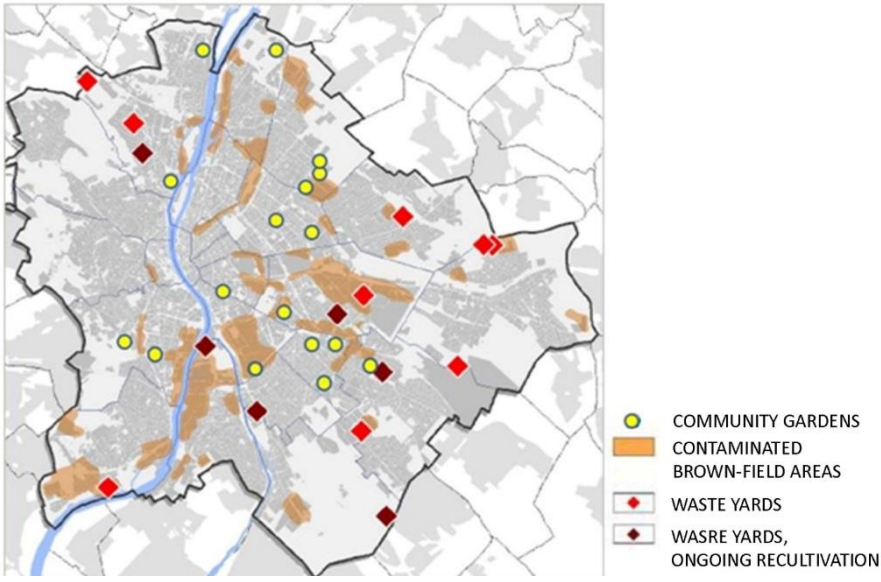

Figure 6. Budapest – soil contamination in brownfield areas

4. Discussion and conclusions

The presented territories can confirm that the brownfield areas present a great potential in development, their new position in the city enables new functions for them. Besides the buildings' function shift, the open spaces need transformation as well. One of the tools for their renewal as part of interim utilization can be the allotment gardens.

The advantages of the interim utilization and the function of the allotment gardens in the brownfield revitalizations is the strong community-building effect requiring low expenses while also improving the environmental quality of the area and the intensity of the greeneries.

Based on the examples examined, we can say that the community gardens demanding everyday presence will require more functions to be implemented, which can be recreational, cultural, and educational as well. A remarkable example is the agricultural park. Newly emerging needs during usage can give new directions to the brownfield redevelopments.

Based on the current research, our future aim is to examine which functions can be implemented in Budapest and which territories are suitable for these. It is also important, however, for the receptive social layer to be present besides the right territorial characteristics. Our research shows that the population density, social composition, and the underused brownfield areas together present the best potential for creating community gardens.

The research on the utilization of underused railway areas of Budapest could also be helpful [12]. Other temporarily utilized brownfield areas can be also connected to the radial-ringed greenery system formed on such railway territories. It would be worthwhile to examine that in the case of a project implementation which of the previously isolated areas become accessible again and thus usable for agricultural parks.

There are many possibilities and there is much to do. This article forms the basis of a common research that asks for a new system of criteria for the brownfield developments of Budapest.

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Figures

Figure 1. Berlin.Tempelhof, source: http://www.vincentkompier.de/wp-content/uploads/2014/05/tempelhof-Foto-Annemieke-Hendriks.jpg [13.07.2015].
Figure 2. Scheduling plan; Concept plan: Andrea Sipos: The temporary utilization of the Nyugati Grund, source: Thesis, Consultants: Dr. Balázs Almási, Krisztina Deák; Corvinus University of Budapest, Faculty of Landscape Architecture, Department of Garden and Open Space Design, 2014.
Figure 3. Berlin. Brownfield at Moritzplatz, summer 2009; "revitalization" Pinzessin-enengärten, summer 2014, source: http://prinzessinnengarten.net/wpcontent/uploads/2009/07/brache. jpg [14.07.2015].
Figure 4. Budapest. Kerthatár – Community garden at Határ Street, source: https://www.facebook.com/KerthatarKozossegiKert [13.07.2015].
Figure 5. Budapest. Dwelling areas according to the way of building-in, source: ITS Budapest stratégia 2020 (2014).
Figure 6. Budapest. Soil contamination in brownfield areas, source: ITS Budapest stratégia 2020 (2014).

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Landscape function analysis as a base of landscape visions

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Abstract: An essential condition for the success of rural areas is the harmonious enforcement of ecologic, economic, and other educational, cultural, aesthetic goods/ services of landscape, diversity of landscape functions. Landscape function analysis is a useful tool for the complex evaluation of rural regions. Using statistic and spatial data, we explored the landscape resources, potentials, and limitations of two pilot regions. But what about the future? Based on the landscape function analysis, we have defined special types of regions/landscape visions according to the long-term ability to retain population by the comparison of economic, production, and habitat value of the landscape.

Keywords: landscape scenario, population retention capacity, micro-regions of Gönc, Csorna

1. Introduction

There is always more attention paid to rural development and rural landscapes. In our study, we apply landscape function analysis using complex landscape indices to explore the potentials and limits of the landscape. Furthermore, based on the landscape function analysis, we formulated special landscape types reflecting the population retention capacity in the long run.

Nowadays, the terms of ecosystem services and landscape functions are frequently used terminologies within the scientific community. In our study, we prefer the use of landscape functions because it has originated principally from

landscape ecology and planning [1, 2]. Furthermore, this concept as an integrative framework integrates natural, economic, social sciences and policy sectors. Landscape services are often defined as "the capacity of the landscape to provide goods and services that satisfy human needs, directly or indirectly" [3].

The term of ecosystem services is rooted in the field of ecology and was originally designed for the assessment of (semi-)natural ecosystems [4]. There are a number of options to group assets offered by nature [4, 5, 6, 7]. There is a consensus about four groups of services: provisioning services (food, timber, etc.), regulating services (climate control, water purification, etc.), supporting (soil formation, nutrient cycling) and information services (recreation, education, etc.). Finally, de Groot distinguishes carrier functions, which include cultivation, habitation, and transportation [6].

The term of landscape functions has been developed parallel with the term of ecosystem services in other scientific fields. Bastian (1997) grouped landscape functions according to the three pillars of sustainability, as production (economic), anthropocentric (society), and regulatory (ecological) functions [8].

In rural regions, people still live from the goods of the landscape (agriculture, tourism) or choose rural settlements for living because of the quality of the environment. Therefore, in rural regions for sustainable development, it is extremely important to analyse the level of landscape functions. As pilot areas, we have two rural regions. According to the classification of the OECD and the EU, both of them belong to predominantly rural areas, where more than 50% of the area's population lives in (rural) communities, where the density of population is under 120 inhabitants/km^2 [9].

The landscape function analysis is the first step in our research project to detect differences of population retention capacity between different types of landscapes. Landscape function analysis is an appropriate tool to explore landscape resources, potentials, and limitations of the present state in rural regions and related landscapes. For rural development, it is an extremely important question whether we are capable to maintain sustainable development in the long run. In the population retention capacity of rural regions, besides the maintenance of the ecologic values, it is inevitable to ensure and maintain a proper, competitive income level. Agriculture and food industry are still a crucial pillar of the economy and employment of rural regions. Furthermore, in a major part of rural regions, villages become especially residential areas from where people commute to the central cities. As an example, we used the multidimensional model for the assessment of the ecologic stability of landscapes, elaborated by Antonio Gomez-Sal and his fellow researchers [10]. We elaborated characteristic landscape models/scenarios describing the population retention capacity based on landscape function analysis. For our research, we have formulated the following objectives:

- To compare the landscape functions within and in between the pilot areas;
- To create a general scenario model based on the landscape functions;
- To identify these scenarios within the pilot areas;
- To compare the scenarios between the pilot areas and to identify the reasons of differences and similarities.

2. Materials and methods

As the first step of our research, based on the concept of landscape functions, we elaborated complex landscape indicators to compare the level of different landscape services and explore the relation between the landscape use and the economic situation of the analysed regions. For the assessment of landscape functions, we used a wide range of complex indicators (*Table 1*).

Table 1. The structure of the indicator system

Used indicators of the research		
Group of indicators	**Indicators**	**Database**
Ecological	Environmental integrity	Matrix of Koshke based on Corine land cover [11]
	Protected areas of national importance	Proportion of protected areas of national importance
	Protected areas of international importance	Proportion of Natura 2000, Ramsar sites, Biosphere reserves
	National ecological network	Proportion of national ecological network
Landscape aesthetic	Naturalness	Proportion of extensive land use forms
	Diversity	Shannon-diversity index [12]
Production	Arable land potential	Proportion of arable land indicating fertility
	Vine and fruit production potential	Proportion of vineyards and horticulture
	Livestock	Number of livestock
	Forestry potential	Proportion of forest areas
Economic	Economic	Total domestic income per taxpayers and ratio of taxpayers

The used landscape indicators mostly cover all types of landscape services [13, 14, 15, 16, 17]. We used the data of the Hungarian Central Statistical Office and other types of databases (Hungarian Spatial Planning and Development Information System – TEIR; database of national monuments, database of landscape values – TÉKA; Hungarian nature and environmental protection databases – TIR) for the evaluation of the level of the landscape services and the characterization of settlements and sub-regions.

We aggregated the spatial data on settlement level and harmonized them into a common dimension. The values (32+34) of all settlements of both pilot regions

were ranged one after the other. Then the values were divided on a scale from 1 to 10. Therefore, we were able to assess not just the situation of settlements in the pilot area but between the pilot regions in general as well.
The landscape function analysis describes the present state of the pilot regions. We explored the population retention capacity of the landscape following the method of Antonio Gomes-Sal and his fellow researchers. We analysed the relation between the economic, ecologic, and production values and elaborated seven basic landscape types (*Table 2*).

Table 2. Relation between economic, ecologic, and agricultural production dimensions and the population retention capacity of the landscape (based on the model of Gomes-Sal [10])

Economic value	Production value	Ecological value	Landscape scenery/Aesthetic value	Landscape type	Population retention capacity
Low	Low	High	High	Landscape of traditional, environmentally friendly, agricultural production of low intensity	Low because of the low profitability
Medium	Medium	High	High	Environmentally friendly, labour intensive production of high added value with varied crop structure "Multifunctional cultural landscape"	Strong ability to retain long-term population
Low	High	Low	Low, Impoverishing landscape	Intensive (industrial) agricultural landscape	Low because of the low profitability and low need for labour
Medium	Low	High	High	Rich in natural and cultural values, agricultural subsidies, tourism "Naturpark"	Ability to retain long-term population with the subsidies and tourism income
Medium/ High	Low	High	High	Suburban landscape of high environmental quality. Strong relation of city and neighbouring villages, controlled building activities	Strong ability to retain long-term population
Medium/ High	Low	Low/ medium	Low	Suburban landscape consuming its natural capital and values. Agglomeration zone, uncontrolled building	Important to stop the loss of ecological values
Low	Low	Low	Low	Degraded landscape. Landscape rehabilitation is needed	Low population retention capacity

Following this model, we have defined characteristic regions in the study areas on the basis of landscape function analysis and estimated the long-term population retention capacity.

We have chosen two rural regions lying along the western and north-eastern borders of Hungary. Both pilot regions contain backward settlements, suffer from severe depopulation processes, and are peripheries or have peripheral parts.

The micro-region of Csorna is situated in the Small-Plain between the great centres of Győr-Moson-Sopron County. The micro-region of Csorna holds most of the settlements of Hanság and Rábaköz (intensive agricultural landscape) together. The wetlands, swamps, and forests of Hanság and the banks and gallery forests of River Rába are of great ecological value and are part of the Fertő-Hanság National Park.

In the micro-region of Gönc, the settlements belong to the most disadvantaged areas of the country. The sample area can be divided into two main parts with different landscape characteristics, the upper valley of the Hernád River and the mountains of Zemplén. The subject area consists of two small towns (Gönc and Abaújszántó) and 30 villages grouped around the towns.

If we consider the natural and economic conditions, we have chosen two characteristically different micro-regions: Gönc lies in one of the most backward regions and Csorna and its surroundings in the second richest region of Hungary. However, Southern Rábaköz can be characterized as an inner periphery with decreasing population.

3. Results and discussions

The research results allow a detailed comparison of landscape functions between the pilot regions and a sub-regional analysis as well (Figure 1); based on the simplified comparison analysis of landscape functions, we defined the landscape visions.

Results of landscape function analysis

The ecological indicator shows characteristic differences in both pilot regions. Settlements of Hanság and Tóköz dispose of high natural variety, high rate of semi-natural, natural vegetation and protected areas, low or medium intensity of cultivation, diverse land use, small patches of meadows, forest belts and plough fields. Up till the 18th century, Hanság was a vast marshland, but following the drainage works most of the lakes of Hanság and Tóköz disappeared with a few exceptions. The preserved marshlands and lakes are, as strictly protected areas, part of the Fertő-Hanság National Park. Meanwhile, Rábaköz is characterized by a high intensity of agricultural production, which leads to a monotonous landscape with low ecological value. In Rábaköz, the only exceptions are the settlements along

River Rába, where a narrow belt of gallery forests and meadows provide high biodiversity (Rábasebes).

In the *micro-region of Gönc*, the Landscape Protection Area of Zemplén, which is one of the most undisturbed and undetected regions in Hungary, has high ecological values, while the agricultural landscape of the Hernád Valley has lower values, where we can witness the lack of the Ecological Network. The lack of the ecological corridors between the core areas (in the mountains and along the river) means that the ecological system cannot work as a real network.

The indicator of landscape aesthetics shows similar values to the indicators of landscape ecology in both pilot regions (*Figure 1*). In the *micro-region of Csorna*, the values of naturalness are high in the settlements of Hanság and Tóköz and mostly low in Rábaköz.

In the *micro-region of Gönc*, the indicator of naturalness shows similar results to the indicator of environmental integrity. The settlements, located in the Mountains of Zemplén, reached high values (e.g. Baskó, Regéc, Mogyoróska, Telkibánya), while the settlements with large cultivated areas have got low values (Felsődobsza, Vizsoly, Vilmány, Pere).

In the micro-region of Csorna, the share of agriculture in economy, employment, and land use is above the national average. Rábaköz is characterized by intensive agriculture. The ratio of plough-lands is extremely high in the micro-region (national average: 48%; local average: 66%, with great local differences). Hanság and Tóköz are characterized by low and medium intensity of agriculture. Fruit production is not characteristic either, but there are a few large plantations. Forestry is not important in the region. Most of the forests are situated in the marshland of Hanság (high values of indicator in Csorna) or along the River Rába (Vág, Páli).

Based on the indicator of agricultural potential, we can also divide *Gönc micro-region* into two significantly different parts. In the Valley of Hernád, the ratio of arable land is very high. This region was historically called as the "pantry of Kosice"; so, agriculture has a great tradition here. Meanwhile, the settlements in the Mountains of Zemplén have very small agricultural areas due to the huge forests. The southern settlements of the micro-region belong to the "Tokaj Wine Region Historic Cultural Landscape" World Heritage Site. The other interesting area is Gönc and the settlements in its surroundings, which are traditionally fruit production areas ("pálinka of Gönc").

In Gönc micro-region, the result of forestry indicator is more or less the inverse of the indicator of arable land potential results. The settlements situated in the Mountains of Zemplén reached a high value of forestry potential. In their economy, forestry has an important role.

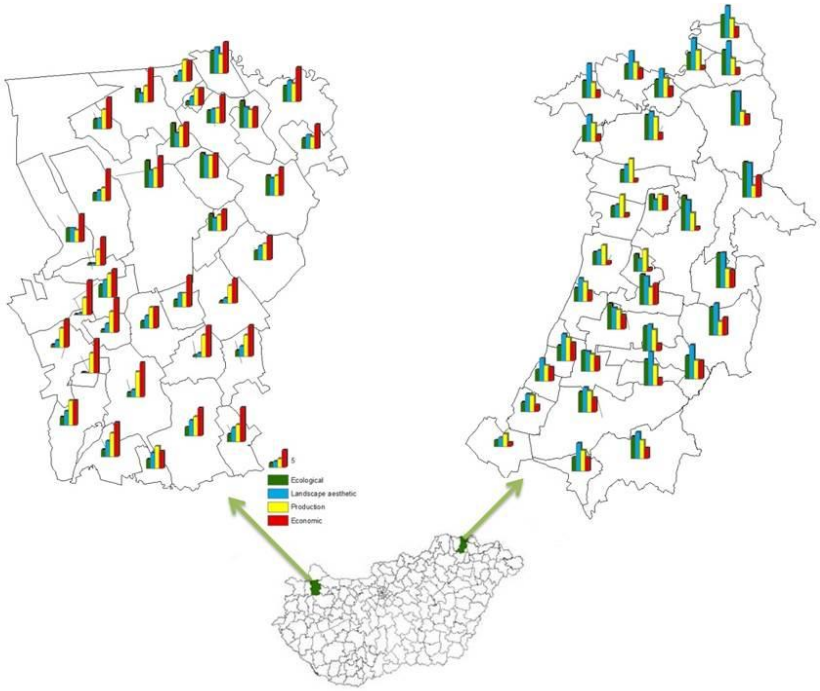

Figure 1. Level of the four value groups regarding the settlements of micro-regions Csorna and Gönc (green – ecological indicator, blue – landscape aesthetics, yellow – agricultural production, red – economy)

Figure 1 also highlights the unfavourable economic situation of most of the settlements in the micro-region of Gönc and in the southern settlements of Rábaköz. In *micro-region Csorna*, the city of Csorna, Bősárkány, Győrsövényház, Kóny, Bősárkány, and Szilsákány have the highest values of the economic indicator. From the point of economic development, the northern part of the micro-region can also be divided into two parts. The settlements of Tóköz neighbouring Csorna have unfavourable values. In the eastern part of Tóköz, in the vicinity of the county seat, the settlements are popular and developing. In *micro-region Gönc*, the settlements in the Mountains of Zemplén have got relatively high values of the indicator. The economy of these villages is mainly based on tourism, wine production, and forestry. In general, the smaller villages in the Valley of Hernád have got the biggest economic and – related to this – social problems.

Summarizing the results of landscape function analysis, we can see that the functioning of several landscape services is insufficient in Rábaköz: the level of

economic, biotope, cultural, and aesthetic functions are below the optimum. High values can be mostly found just in the settlements of Eastern Tóköz and Hanságmente.

"Landscape visions" in the pilot regions

The relation between ecological and economic aspects, especially the harmony between them, is extremely important in the sustainable development of rural regions. We consider agricultural production also important because it is one of the most important human activities which transform nature, and it reflects developed or less developed techniques and processes, while it also needs investments in materials and energy. The productive system significantly influences landscape aesthetics. Based on the ecological, economic, and production performances of the pilot regions, we looked for the model scenarios (*Table 1*). We found several landscape types in the pilot regions (*Figure 2*).

The micro-region of Csorna

– **Tóköz 1**, **Hanságmente**: *Suburban landscape of high environmental quality*

Settlements of favourable economic situation with high natural value and less intensive agricultural production (good availability) belong to this group.
With the current trends, the maintenance of the present level of population retention capacity is possible in the long run, population growth is expected.

– **Tóköz 2**: *Landscape of traditional, environmentally friendly, agricultural production of low intensity*

Settlements of unfavourable economic situation with high natural value and less intensive agricultural production (poor availability) belong to this group.
According to the current trends, population retention capacity cannot be maintained, population loss is expected. Reversal of the current trends is possible by strengthening the central (service, supplying, job-creating) functions of Csorna (agglomeration character, suburban landscape) or by converting limitations into advantages promoting ecological farming, ecotourism reaching the "nature park" character.

– **Rábaköz 1**: *Intensive agricultural landscape (weak multifunctional character)*

Settlements of relatively favourable economic situation, primarily agricultural character with significant industrial, commercial activity and medium ecological value belong to this group. With the current trends, the maintenance of the present level of population retention capacity is possible in the long run; the favourable processes can be strengthened by promoting multifunctional agricultural production and food processing.

– **Rábaköz 2**: *Intensive agricultural landscape*

Settlements of agricultural character in unfavourable economic situation belong to this group. The current trends cause population loss. The unfavourable trends can be moderated by strengthening the central (service, supplying, job-creating) functions of local centres and promoting multifunctional agricultural production and food processing in the region. Furthermore, the ecological development of the region is inevitable.

– **Rábaköz 3**: *Landscape of traditional, environmental friendly, agricultural production of low intensity*

Settlements of unfavourable economic situation with high natural value (Vág, Rábasebes) belong to this group. According to the current trends, population retention capacity cannot be maintained, population loss is expected; the unfavourable processes can be moderated by improving availability and promoting multifunctional agricultural production and ecotourism.

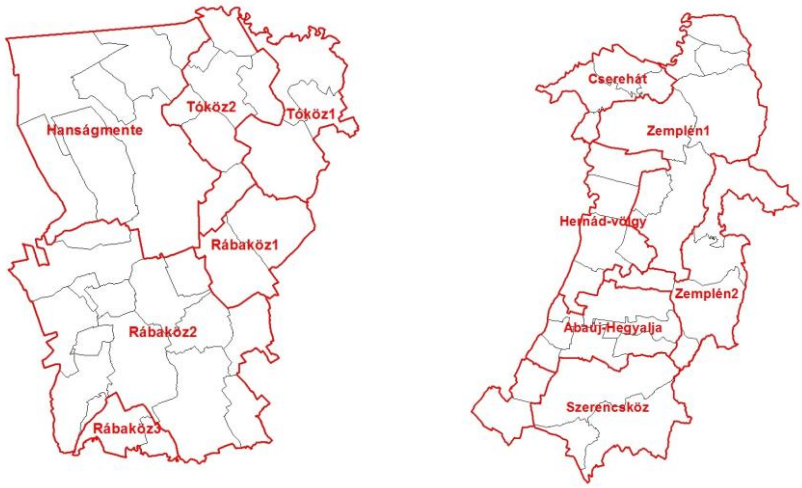

Figure 2. Landscape types in the pilot regions

The micro-region of Gönc

– **Cserehát:** *Basically, industrial agricultural landscape and partly natural values consuming suburban landscape features*

Agricultural settlements with low economic and ecological value but with good accessibility belong to this group. Mining is important in the region (gravel mines

along the river). Landscape aesthetic value is relatively high because of the semi-natural Hernád River. Population retention capacity is average (locally low employment needs, but good availability). The population can be sustainable, but more attention will have to be paid to ecological values.

- **Zemplén 1:** *Multifunctional cultural landscape with tourism and traditional, environment-friendly agriculture and forestry*

Settlements of average or poor economic situation and of high ecological and landscape aesthetic values (Zemplén Mountains, Landscape Protected Area of Zemplén), settlements of average or rather high production value belong to this group. Forestry and labour-intensive fruit production are important in the region.
The long-term population retention capacity is high (high labour demand in the environmentally friendly agriculture, fruit production). Favourable processes can be fostered by the further development of tourism.

- **Hernád Valley:** *Industrial agricultural landscape*

Settlements of agricultural character in unfavourable economic situation belong to this group. Population retention capacity is low (low labour demand); the current trends could be changed by switching the industrial agriculture to a more sustainable and multifunctional way of production (environmentally friendly agriculture, organic farming, landscape management in flood-plain areas). The River Hernád also meant a very good basis for tourism (further development is recommended).

- **Zemplén 2:** *"Naturpark" scenario (tourism and forestry, high number of natural and cultural values)*

Settlements in good economic condition with high ecological and landscape aesthetic values belong to this group. Cultivation is of medium intensity, based on forestry, almost no agriculture, with the exception of the gardens and small orchards around the villages. Population is decreasing because of poor availability. Thanks to the natural resources, this trend could be turned back by further development of (nature-based) tourism and clustering, sustainable forestry, high labour demand, handicrafts and food productions (honey, marmalade, etc.).

- **Abaúj-Hegyalja:** *Multifunctional cultural landscape with some traditional, environmentally friendly agricultural features*

Settlements of high level of ecological and landscape aesthetic values (Zemplén Mountains; cultural scenic values) with high cultivation intensity (orchards, high percent of arable lands) belong to this group. The economic value is average or below average because of the low profitability of the present agriculture.
Unfavourable processes can be changed by promoting labour-intensive organic farming, fruit production, and development of availability.

– **Szerencsköz:** *Multifunctional cultural landscape with some natural values consuming suburban landscape features*

Settlements with average level of ecological and landscape aesthetic values belong here – production value is high (wine production, Tokaj Wine Region UNESCO World Heritage). The relative good availability and profitability of wine production ensures average economic conditions. For maintaining the relatively good population retention capacity, more attention will have to be paid to environment protection (especially regarding mining). Besides, we recommend a more effective utilization of cultural values and tourism development based on traditional (labour-intensive) viticulture.

As *Figure 2* shows, we can find almost all scenario models in both pilot regions, with the exception of degraded landscapes. In the micro-region of Gönc, there are several types of landscapes with positive population development trends (multifunctional landscape, nature park); meanwhile, in Csorna, we have found just suburban landscapes with high natural values. In both pilot regions, there are landscape types causing negative population trends: industrial agricultural landscape and landscape of traditional, environmentally friendly, agricultural production of low intensity.

4. Conclusions

Despite the different economic situations of the pilot regions, we have found similar correlations between landscape functions and the population retention capacity of the landscape. Sometimes we cannot find clearly the presented scenario models, as our pilot regions also show it. However, we can adjust the state of rural regions to these models which can help to detect the cause and driving forces of negative trends, and within the frames of rural development we can take effective steps to stop them.

The land use system of a rural region can maintain the population retention capacity in the long run in case it can ensure the ecological, economic, and social aspects so that a balanced functioning of landscape functions is favourable. We have witnessed low population retention capacity in the case of high production value with low economic, ecological, and aesthetic values (Hernád Valley, Rábaköz). The "industrial," monotonous agricultural production does not offer appropriate economic base for rural regions because of the lack of labour-intensive production types, products of low level of processing, limited scale of complementary activities, etc. The diversification of the structure of agricultural production could enhance population retention capacity in the pilot regions.

Multifunctional cultural landscape with diverse production structure could be the priority of rural development for these regions.

In the case of low economic but high ecological and aesthetic value, which characterizes landscapes of traditional, environment-friendly, and agricultural production of low intensity, the model of "nature park" can show the priorities of rural development: promoting ecological farming, ecotourism.

In landscape evaluation, by the application of indicators, we can usually highlight just a small fraction of the complexity of the landscape. For a more detailed analysis or for correction, it is possible to involve a wider range of indicators. In scenario analysis, the relative state of the regions and the determining trends are important. The method is applicable especially to rural developments to formulate visions of the landscape and to highlight the possible negative trends. Such analyses can help to develop effective rural development and landscape management programmes in order to reach positive visions. Further researches for other pilot areas in Hungary and international comparative analysis in other countries enable the improvement and refinement of the method.

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Postmodern landscape architecture: theoretical, compositional characteristics and design elements with the analysis of 25 projects

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Abstract: This paper endeavours to highlight three aspects of postmodern landscape design: theoretical basis, composition and design elements. Postmodern theories, philosophy influenced the language of the postmodern landscape architecture and got materialized in the use of narratives, eclecticism, the Rhizome-principle. Postmodern landscape composition can be associated with anti-hierarchy, unusual structures, landforms, and playful moods. Postmodern design elements consist of the strong graphical use of colour and pavements, bizarre water features, unusual structures and buildings, postmodern sculptures and thematic garden details. 25 analysed projects try to capture the essence of postmodernism in landscape architecture as well as to reveal points of intersection within these projects.

Keywords: landscape history, landscape design, comparative analysis

Introduction

There are numberless works discussing postmodernism, but, if we view these in relation to landscape architecture, we will soon realize that there are many gaps to be filled. This fact is even more intriguing since one of the best known theorists of postmodernism, C. Jencks, whose famous gardens, landscape designs have made him one of the leading figures in British landscape architecture, discusses postmodernism in *The Language of Post-Modern Architecture* solely from the perspective of architecture [1]. Scientific publications regarding postmodernist landscape architecture of the 1980s and 1990s are almost non-existent.

Our research was inspired by descriptive modern–postmodern opposite pairs such as *romanticism–dadaism, form–antiform, purpose–play, hierarchy–anarchy,* by I. Hassan [2] and *utopist–popular, izotropic space–varied space, simplify–complexity*, and *integration–collage* by C. Jencks [3]. In addition to this, aspects of analysis were determined by postmodern philosophical ideas.

Material and methods

This paper is based on the analysis of 25 landscape architecture projects established between 1974 and 2000, which can be discussed parallel with postmodern architecture. We examined these projects through three main aspects in 19 subcategories: postmodern *philosophy (7), composition (8), and design elements (4)*. The goal of the comparison is to get quantitative results, how much these aspects describe postmodernity in landscape architecture, and which examples can be clearly defined as postmodern masterpieces.

1. Postmodern philosophy: narratives, indetermanency, self-realization, pluralism, rhizome principle, playful

In the following part, we introduce 7 basic theoretical issues, which are deeply discussed in various postmodern theories (reference mentioned below). Each of these is represented in the quantitative analysis (*Table 1*) with 0-1-2-3 points.

a, Narratives | Lyotard talks about the end of '*grand narratives*,' *or metanarratives*, which characterized the history before postmodern. He professes a preference for this plurality of small narratives that complete each other. Postmodernists attempt to replace metanarratives by focusing on *specific local contexts* as well as the diversity of human experience. [4] Lyotard recommends replacing grand, universal narratives with small narratives what is also visible in some landscape architectural compositions.

Examples: One of them is the most well-known postmodern icon: *Piazza d'Italia*, which has some small narratives from renaissance to baroque as well. Next to the past, there are some local narratives to the Italians who live there, and there is an ironic personal narrative aspect: a sculpture about Charles Moore, the designer itself. A. Isozaki designed the *Tsukuba center*, which carries several levels of small narratives. In the middle of the public space, there is the Daphne tree from the Greek–Roman mythology. The space context is the pattern of Rome's Campidoglio and, what is more, it follows the model of Ledoux's Ideal city. *Jacob Javits Plaza* would be demolished during the waterproofing construction; the opportunity was seen to revitalize the plaza. During the time that R. Serra's "Tilted Arc" inhabited the plaza, this 14-foot-high sculpture was an obstruction both

visually and physically to pedestrians. This performance determined the history of the plaza's place that M. Schwartz evokes again with the green snake-formed benches.

b, Indetermanency | Critics have more or less reached a consensus regarding Modernism; it has become a well-defined aesthetic concept with clear-cut definitions and characteristics, and hence easily recognizable. However, according to I. Hassan [5], while modernism is characterized by *centring*, postmodernism is characterized by *dispersal*, by deconstruction and it is based on the view of the world devoid of a centre. To describe it, Hassan has introduced the concept of "indetermanency: by ~, or better still, indeterminacies, I mean a combination of trends that include openness, fragmentation, ambiguity, discontinuity, decenterment…" These trends are presented in the particular examples of the elements of landscape design as well as on the level of conceptualization.

Examples: The red follies of *Parc de La Villette* [6] are the best-known elements, which represent the deconstruction theory of French philosopher J. Derrida. The separation of elements, structures and re-form meant new experiments in design. The indetermanency is based on the contrast between the park's old and futuristic buildings and between the conventional and unconventional forms, elements. In the design of the *Parc André Citroën*, these contrasting trends envisage bringing together six small themed "Serial Gardens," and a big unified central space. The manifestation of indetermanency in the *Millenáris Park* (Budapest) can be found in the duality of *interactivity and passivity*, in the designed programme of the park which creates the effect of annihilating one another.

c, Self-realization | S. Freud dwelt on the unconscious aspect of the human psyche: the conscious is a smaller part of the psyche, while the unconscious is where our instincts, desires are at work. [7] The tenet that human beings are unable to grasp what goes on in their unconscious mind contributed to the change in how humans are viewed. Human beings are not pre-determined; each human being contains the germ of becoming more "than they are, of becoming 'special' ". Thus, creativity acquires paramount importance: the impossibility "to know thyself" goes hand in hand with the possibility of the existence of hidden talents, and postmodernists have taken up this idea by putting emphasis on self-fulfilment.

Examples: The essence of self-fulfilment within landscape design can be best grasped through the works of M. Schwartz. It is no coincidence that her statement "Anything goes!" has become the slogan of postmodern landscape architecture. Two of her creations underline this free, open-minded attitude: the *Whitehead Institute* [8], which is based on the distorted Siam-joint of a French Renaissance and a Japanese Zen garden. The elements that compose these gardens have been distorted. All the plants in the garden are plastic. The clipped hedges, which double as seating, are rolled steel covered in Astroturf. The green colours, which are the

strongest cues that this is a garden, are composed of coloured gravel and paint. The intent was to create for the scientists who occupy this building a visual puzzle that could not be solved. The garden is an ode to "better living through chemistry". At *Jacob Javits Plaza*, the benches swirl around the "topiary," or 6-foot-tall grassy hemispheres that exude mist on hot days. P. Walker's works are very individual as well: the *South Coast Plaza Town Center*, the *Children's Pond and Park*, and the *M. Luther King Promenade* have a particularly strong personal-taste design.

d, Pluralism | The clarification of postmodernism begins with rejecting the universal models, the a priori values, and by publicly accepting pluralism as the main goal. Postmodernism bypasses the distinctiveness which has been a characteristic of avant-garde and neo-avant-garde art: postmodernism accepts several conceptions, even those which contradict each other and urge to accept the coexistence of different styles [9]. The projects examined display the elements of the old, traditional style as well as those of the contemporary one.

Examples: The *Parc de Bercy* displays the coexistence of the old and postmodern building styles and the landscape is a projection of this pluralism in the architecture. Consciously cumulated historicism appears in the case of the *Tsukuba Center* and the *Whitehead Institute*, the common element being the use of Asian landscape design elements together with those belonging to the classic European styles. The *Bürgerpark Saarbrücken* also combines the ancient Italian elements of style with those of the local industrial premises. The park of the *Hotel Kempinski Munich* is a wonderful example of how the parterre of the French Baroque castles is rethought in an up-to-date way.

e, Rhizome principle | Rhizome takes its name from plants that spread via a connected underground root system. As a metaphor, G. Deleuze and F. Guattari [10] used rhizome to refer to a non-hierarchal form of organization. They used the term "rhizome" to describe theory and research that allows for multiple, non-hierarchical entry and exit points in data representation and interpretation. A rhizome works with horizontal and trans-species connections, while an arborescent model works with vertical and linear connections. In our research, it can be translated more than anti-hierarchy because there is a strong connection between elements, components.

Examples: The *Piazza'd Italia* is a famous outdoor stage, and the elements of the scene have a very strong connection. It is the same situation with the elements of *Whithead Institute* (the light green forms and surface continue in vertical direction as "a vertical garden") or the *DNS Garden* with the five human sense organs, where elements are integrally connected to each other.

f, Playful | The principal characteristic of formal and thematic experimentation – and the other important drive in postmodernism – is playfulness. Playfulness is not to be viewed purely from a formal standpoint; it has acquired a deeper meaning with the postmodern [11]. This key-expression has to be viewed as

an answer to doubt. Postmodernists create their own independent worlds (exactly as in a game), which in their elements resemble the real world (they use the elements of the real world) and are at the same time very different from it. We have reached the conclusion and want to shed light on the intrinsic connection between playfulness and the design based on self-fulfilment.

Examples: Playfulness is generally present in landscape architecture on a smaller scale – as in the wavy motif of the finishes, winding paths and the wavy pattern of the space in the *Jardin Atlantic*. Benches, lighting, and their unique design are gaining ground and they also contribute to the playful mood. The red crane-like lighting fixtures in *Schouwburgplein* can be operated by remote control and are a good example to illustrate this statement. Statues in the open space also belong to the elements that are able to conjure up the world of playful design: the big red amorphous statues of the *Parc de Coudrays*.

2. Postmodern composition: brown field, collage, antihierarchy, thematic garden details, diagonal, different ground levels, unusual water architecture, unusual structures, landforms

Postmodern landscape architecture tended to find new forms of expression, new visual methodologies. A significant number of these projects are experimentations. This period has served as an 'experimental lab' in landscape architecture, bringing forth new compositional issues and new elements. We highlighted 8 physical characteristics referring to the composition of the whole.

a, Brown field, based on industrial area | In the second part of the 20th century, according to post-war urbanization, former huge industrial territories lost their original functions; so, they became potential areas for city-developments around the 70s-80s.

Examples: Park la Villette built on former cutlery – as the main halls reminds us; *Park Citroën* on a former car-industry plot, where the spatial arrangement of the building refers to the factory halls; *Park del Clot*, *Jardin Atlantik*, and *Millenáris* are on former railway industrial sites, stations. This fact corresponds with historicism and past narratives, while conserving some of these industrial heritages helps to display collage compositions.

b, Collage | The collage as a spatial-orientation compositional method tries to demolish the inner coherence, the unity. Details will individualize themselves. The collage space can be reflected horizontally as well as vertically.

Examples: La Villette might have been the first design consciously using this collage structure: the three layers (areas, directions, and points) overlap vertically. *Parc des Coudrays* is a good example for horizontal collage: the first layer is the vegetation, the second one the edge-border-relief, third are the areas, and the fourth

is the network. A flat, one-level collage can be seen on *Cambridge Center Garage Roof Garden*, the *Piazza d'Italia*, and the *Tsukuba Center*.

c, Anti-hierarchy | One of the key characteristics of modern design is the hierarchical organization, the order. Postmodernism denies this by emphasizing the co-ordination and coequality of each compositional element. Almost all the examples underline this feature.

Examples: As early examples, the *Franklin Court* and the *Welcome Park* show late-modern characters (symmetry, hierarchy, centre-located house-imagination sculpture of P. William). Both examples are designed by R. Venturi, who determines the key feature of postmodern architecture in his book [12], but he can hardly realize these aspects on his open-space design, which will be clearly visible on the evaluation table.

d, Thematic garden details | Topic/theme-oriented park parts bring something new to the former sports and leisure activities. The concept can refer to philosophical, aesthetical, and esoteric content or can imply the local (industrial) history of the location.

Examples: The boscé garden enclosures of *Park Citroën* have metaphoric relation to the days, planets, colours, and therefore to the planting schemes. *Jardin Atlantik* also has a *Wavy plant room, a Humidity room, a Blue and mauve room, a Room of mirrors, a Silence room, and a Stone pavilion*. The planting with its character and colour refers to the Atlantic Ocean. At *Parc del Clot*, the former hall was transformed into a mediaeval Islamic inner courtyard as a silent meditative part in between the park zones.

e, Diagonal | Great, long diagonals are a counter-reaction to the orthogonal and perpendicular calmness of Modernism. It gives tension and asymmetry to the space, while it allows a simple, fast cross-cut for pedestrians. This feature is a classical postmodern invention and has been taken over by the contemporary design.

Examples: The most well-known great diagonal is present in the "classical" Parisian postmodern public parks as *Parc de La Villette, Parc de Citroën, Bercy Parc*, and in *Parc del Clot*, but it is absent in many other cases.

f, Different ground levels | The raised-lifted and recessed-sunken platforms are also contradictory to the horizontal editing of modern architecture. This playful spatial feature of elevated walkways, promenades, terraces, or sunken sports grounds creates a higher variety of spatial experiences by multiplying the view, vistas, and orientation points.

Examples: The prototype was again the hanging promenade of *Park la Villette* along the channel, but the two main diagonal axes of *Parc del Clot* also underline this complex elevations by varying its height circumstances from the floor, mounds, and fencing. A nice sunken space is the amphitheatre of *Tsukuba Center* or the southern entrance zone of *Parc Citroën*.

g, Unusual water architecture | The modern design rather used relaxed mirroring pool surfaces as horizontal forms or gentle water jets, but in postmodern design the unusual, shocking water features are often associated with astounding sculptures, open-air installations, where the dynamic of the water has strong emphasis.

Examples: In *Jardin Atlantik*, the sculpture *Ile des Hesperides* (J.-M. Llorca) is not only a mythological reference but a fountain as well, which provides space for meteorological equipments. In the sunken courtyard, *Parc del Clot*, the water channel sculpture of B. Hunt is to be seen, while the façade of the former industrial building has been transformed into a huge rapid waterfall.

h, Unusual structures, landforms | A kind of collision (contraposition) is also typical next to the experimental-attempting approach of postmodern design. The listed examples have various strange and extraordinary (built) structures, landforms. This is also a crucial compositional invention of this time, which is in a common design tool of the contemporary palette.

Examples: Turf sculptures of Jencks' Portrack House, the huge turf-mounds of *Parc des Coudray*, the smaller hemispheres of *Jakob Javits Plaza* or the long linear dam-dune forms of *Millenáris* are great examples longing for new space-, material-, and colour-use [13].

3. Postmodern design elements: graphical colour use, geometrical pattern, Various materials

The design elements are easily correlated with specific developments or movements within the postmodern. Although there has been a strong tradition from the early nineteenth century, postmodern has changed and showed a surprising transposition of their radical ideas onto the three-dimensional space.

a, Graphical colour use | There is one individual colour of *Piazza d'Italia* (brown), the *Whitehead Institute* (white-green), and *Jakob Javits Plaza* (light green) too. Postmodern landscape architecture was brave to use red or other surprising vivid colours and high contrasts.

b, Geometrical pattern | Some postmodern examples have an inspiring collection of geometric patterns on the pavement or on the surface. At *Tsukuba Center*, after using geometrical grid shapes with vivid colour, the design becomes a simple yet wholly striking work. *Piazza d'Italia, Cambridge Center Garage Roof Garden, Children's Pond and Park, Martin Luther King Promenade, and Schouwburgplein* also have individual geometric surfaces.

c, Various materials | Next to unusual materials, the most important character of postmodern material use is the industrial choice of material. The unusual structures and sculptures are often made out of metal: red follies in *Parc de La Villette*, Daphne's trees at *Tsukuba Center*, white cubic pavilions at *Cambridge*

Center, Hesperides fountain at *Jardin Atlantik*, or outdoor lighting at *Schouwburgplein*. All of these strengthen the effect of indetermanency, playfulness, and unusualness.

Results and discussions

After the visual, design-oriented description of the sites, we deeply examined the 25 listed projects with simple evaluation according to the listed characteristics *(0: not typical – 3: very typical, see Table 1.)*. The complex database sheet underlines and disaffirms our hypothesis.

Results of theory characteristics: From the average of these aspects *(15.7 /21)*, we can conclude that all of these aspects are very typical for the projects *(20 out of 25 examples have above 66%)*; moreover, we can state that *Indetermanency*, *Self-Realization*, and the *Rhizome Principle* were the most characteristic categories of philosophy *(2.9)*. This leads to the conclusion that the theoretical background of postmodernism can be very clearly observed in all cases. These aspects are excellent expressions for deeper qualitative description.

Results of composition characteristics: The assumed compositional aspects are more or less characterizing *(14.2/18)* the compositional guidelines. At some cases, only 0/3 answers were given (diagonal, diff. ground level). Anti-hierarchy *(2.8)*, unusual water and terrain features, collages and different ground levels *(2.8)* are mostly common characteristics.

Results on design element characteristics: Results underline that these subcategories are typical of the projects *(10.2/12)*. Especially the graphical pavement and different materials *(2.9)* are most common.

Results on projects' final score: Finally, 15 examples have results above 66*% (40.1/54)*, 8 *even above 80%: Park de la Villette, Park Bercy, Park A. Citroën, Parc del Clot, Tsukuba Center, Piazza d'Italia, Parc de la Espanya Industrial, Getty Centre and Millenáris, South Coast Plaza, Children's Pond and Park, Bürgerpark Saarbrücken, Portrack House, Schouwburgplein, and Jarden Atlantik.* These are all large complex compositions with various design aspects which provide the chance to adapt more features of the era. They were built around 1988. Only 4 of 25 examples did not reach the 50%: *Heritage P. Plaza, Welcome P. Franklin P.*, and *Moody Gardens*. Many of them were built at the beginning of the era, so they rather show signs of Late Modernism (symmetry, order, clearer compositions).

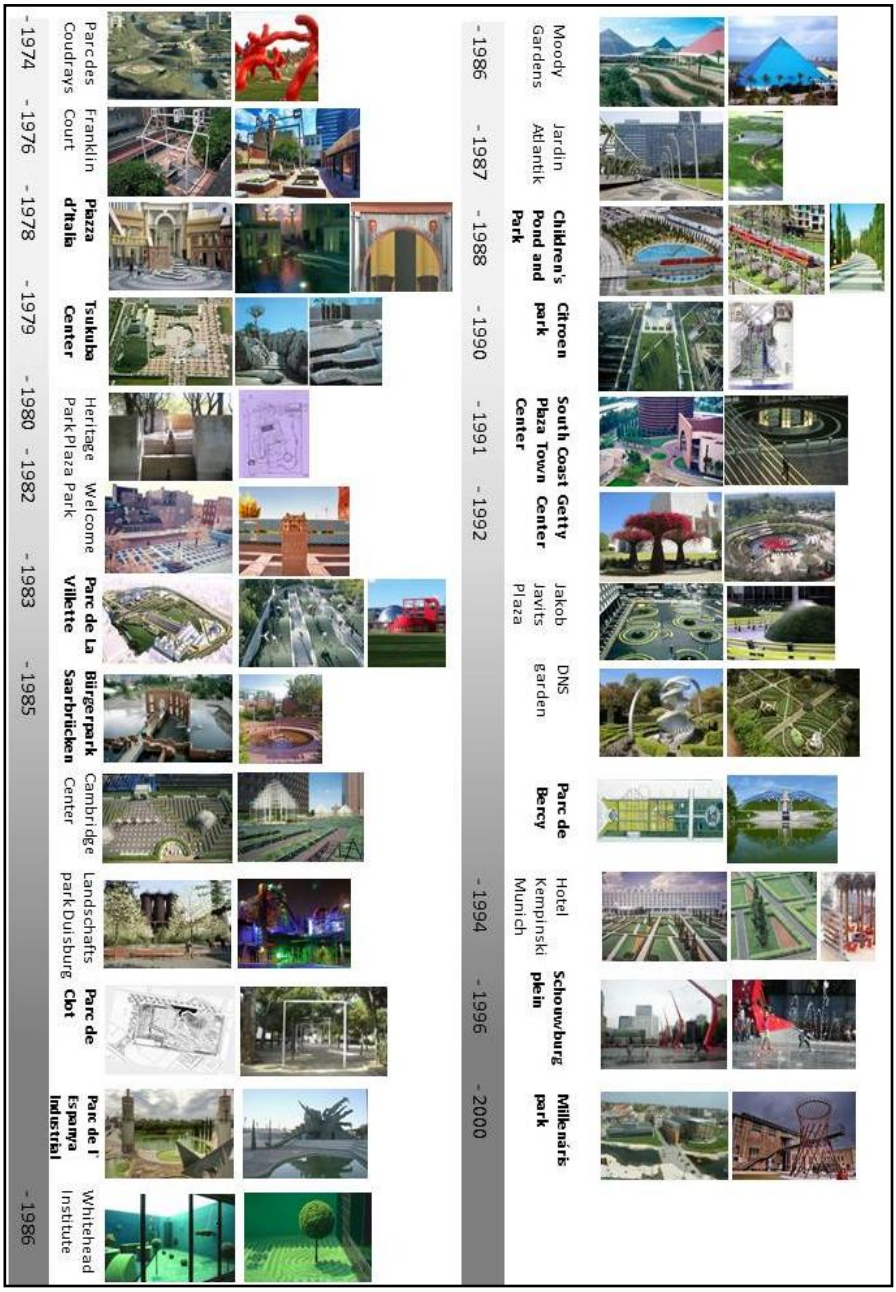

Fig. 1. Chronological order and visual introduction of the examined 25 projects

Date	Name of projects	Landscape architec, team	Location	Postmodern phylosophy: narratives (0-3)	indetermanency (0-3)	self-realization (0-3)	pluralism (0-3)	rhizome principle (0-3)	playful (0-3)	Sum-up (0-21), under 50%, above 66% marked	Postmodern composition: brownfield, fomer industrial area (0/3)	collage (0-3)	antihierarchy (0-3)	thematic garden details (0-3)	diagonal (0/3)	diffrent ground levels (0/3)	unusual water architecture (0-3)	unusual structures, landforms (0-3)	Sum-up (0-18), under 50%, above 66% marked	Postmodern elements, materials: graphical color use (0-3)	graphical pavement (0-3)	geometrical pattern (0-3)	different materials (0-3)	Sum-up (0-12), under 50%, above 66% marked	TOTAL (0-54), under 50%, above 66% marked	Postmodern park/ public space
	The average of each charcteristic			2,2	2,9	2,8	2,4	2,9	2,6	**15,7**	1,3	1,9	2,8	1,2	0,7	1,6	2,0	2,8	**14,2**	2,3	2,8	2,3	2,9	**10,2**	**40,1**	
1980	~~Heritage Park Plaza~~	Lawrence Halprin	Texas, USA	1	1	2	1	2	2	9	0	0	1	1	0	0	3	3	8	0	0	0	0	0	17	no
1982	~~Welcome Park~~	R. Venturi,Scott Brown and Ass.	Philadelphia, USA	2	1	2	2	2	2	11	0	0	0	0	0	0	0	1	1	2	3	3	1	9	21	no
1976	~~Franklin Court~~	Robert Venturi	Philadelphia, USA	2	2	2	1	2	2	11	0	0	0	0	0	3	1	2	6	1	2	1	1	5	22	no
1986	~~Moody Gardens~~	Geoffrey Jellicoe	Texas, USA	3	3	2	1	2	2	13	0	0	3	3	0	0	0	3	9	0	0	0	2	2	24	no
1974	**Parc des Coudrays**	Michel Corajoud	Élancourt, France	3	3	3	2	2	3	16	0	2	3	2	0	3	0	3	13	0	1	0	2	3	32	√
1985	**Cambridge Center Garage Roof Garden**	Peter Walker, M. Schwartz	Cambridge, USA	0	2	3	2	3	2	12	0	3	3	0	0	0	0	3	9	3	3	3	3	12	33	√
1992	**Jakob Javits Plaza**	Martha Schwartz	New York, USA	3	3	3	1	3	3	16	0	0	3	0	0	0	0	3	6	3	3	3	3	12	34	√
1985	**Landschaftspark Duisburg-Nord**	Latz+Partner, Latz-Riehl	Duisburg, Germany	0	3	1	2	3	2	11	3	0	3	0	0	3	3	3	15	2	3	1	3	9	35	√
1994	**Hotel Kempinski**	Peter Walker	Munich, Germany	1	3	3	3	3	2	15	0	1	2	1	0	0	1	3	8	3	3	3	3	12	35	√
1986	**Whitehead Institut**	Martha Schwartz	Massachusetts, USA	3	3	3	3	3	3	18	0	0	3	0	0	0	0	3	6	3	3	2	3	11	35	√
1987	**Jardin Atlantik**	Brun Penna and Schnitzler	Paris, France	2	2	3	2	3	2	14	0	2	3	1	0	3	2	2	13	2	2	2	3	9	36	√
1996	**Schouwburgplein**	West8	Rotterdam, Holland	3	3	3	3	3	2	17	3	0	2	0	0	0	0	3	8	3	3	3	2	11	36	√
1988	**Children's Pond-Park**	Peter Walker	California, USA	0	3	3	2	3	2	13	0	2	3	0	0	3	3	1	12	3	3	3	3	12	37	√
1992	**Portrack house and DNS garden**	Charles Jencks	Dumfries,Scotland	3	3	3	3	3	3	18	0	0	3	3	0	0	3	3	12	1	3	2	3	9	39	√
1985	**Bürgerpark Saarbrücken**	Peter Latz	Saarbrücken, Germany	2	2	2	1	2	2	11	3	3	2	1	3	3	3	2	20	1	3	2	2	8	39	√
1991	**South Coast Plaza Town Center**	Peter Walker	California, USA	1	3	3	2	3	3	15	0	3	3	1	0	0	3	3	13	3	3	3	3	12	40	√
2000	**Millenáris**	Dominika Tihanyi and Partners	Budapest, Hungary	3	3	3	1	3	3	16	3	3	3	3	0	0	2	3	17	2	2	2	3	9	42	√
1992	**Getty Center**	Robert Irwin	California, USA	3	3	3	3	3	2	17	0	2	3	1	0	3	3	3	15	3	3	3	3	12	44	√
1985	**Parc de la Espanya Industrial**	Luis Peña Ganchegui	Barcelona, Spain	3	3	3	3	2	3	17	3	2	3	3	0	0	3	3	17	2	3	2	3	10	44	√
1978	**Piazza d'Italia**	Charles Moore	New Orleans, USA	3	3	3	3	3	3	18	0	3	2	0	0	3	3	3	14	3	3	3	3	12	44	√
1979	**Tsukuba Center**	Arata Isozaki	Ibaraki, Japan	3	3	3	3	3	3	18	0	3	3	0	0	3	2	3	14	3	3	3	3	12	44	√
1985	**Parc de Clot**	D. Freixes,V. Miranda	Barcelona, Spain	2	3	2	2	3	3	15	3	3	3	0	3	3	2	3	20	1	3	3	3	10	45	√
1990	**André Citroen park**	Gilles Clement, A.Provost	Paris, France	2	3	3	3	3	2	16	3	3	3	3	3	3	2	2	22	2	2	2	3	9	47	√
1992	**Parc de Bercy**	Ian Le Caisne and P. Raguin	Paris, France	3	3	3	3	3	3	18	3	2	3	3	3	0	3	3	20	2	3	2	3	10	48	√
1983	**Parc de La Villette**	B. Tschumi, A.Chementhoff	Paris, France	3	3	3	3	3	3	18	3	3	3	3	3	3	3	3	24	3	3	2	3	11	53	√

Fig. 2. Quantitative analysis of the 25 projects, ranked according to their final scores

Conclusions

Postmodern theories are all reflected in the postmodern credo of landscape architecture. The design of open places, squares, as well as parks built between 1980 and 1990 can be best characterized by such terms as narratives, indetermanency, and the rhizome principle. The famous quotations "Anything goes" and "Less is more" are reflected tangibly in these compositions. The postmodern landscape's stylistic language is determined by experimentation and self-realization, unusual personal solutions. To sum up, we can state that postmodern theories manifest themselves not only in art, philosophy, and architecture but emphatically in the landscape design as well. By a simple quantitative grading, the personal aesthetical judges could have been objectified. The study underlined that there is a coherent design language of the era, and the majority of these big design sites can be claimed as examples of postmodern landscape architectural style. The finer details and features of the singular parks require further finer analysis.

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Special aspects of water use in Persian gardens

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Abstract: The Persian garden is one of the most characteristic and notable element in the Iranian landscape. Considering Iran's hot and dry climate along with water deficit for plantation, it becomes noticeable how important the art of making gardens is to Iranians.

Water is one of the most crucial elements in the Persian garden, and we can state that gardens would be meaningless without it. Garden applications use water with its various abilities such as life, brightness, cleanliness, light, inertia, and motion, which bring forward numerous feelings in the human soul and enhance mental comfort. Also, its various running structures, such as basins, streams, water creeks, and fountains, provide mental comfort and technical functions.

Keywords: water system, water feature, decorative elements, functional role

1. Introduction

Among different natural elements, water is one of the most important elements, and it usually influences the other natural factors. Water has a deep relationship with the environment. Fluidity and flexibility make water a life-giving substance. Water offers playful musicality when moving, contemplative reflection when still. The fluidity of water represents the transparency of space and the unity of the garden. Most Iranian gardens are located in a semi-desert or desert – inappropriately for such landscapes: hot and dry weather in the summer season, cold and dry weather in the winter, with very low precipitation (5–25 mm a year).

Donald Wilber wrote in his "Persian Gardens and Garden Pavilions" that the most important reasons for considering the Persian garden as "paradisian sites" are their rich water systems and luxuriant vegetation in an environment characterized by extremely hot weather and arid deserts in Iran. Therefore, a garden is a representation

of paradise and it has held a sacred position in Persian beliefs. Accordingly, a garden is really important in religious trainings before and after Islam [12].

Water has always been deemed valuable in Iran since it was known as the omen of light and purity in ancient Persia. Water running in the four corners of Iranian gardens assimilates the four streams of water in the paradise [2]. In Iran, garden design is water design; Iranian enthusiasm for water has led to its use in various forms such as gardens, the quadrilateral scheme, brooks, low-slope, and winding stream to make the air cool, pleasant, and fresh.

2. Materials and methods

The present paper aims to investigate the importance of the main decorative water features such as pools, fountains, channels, and waterfalls, considering the functional roles of water use in Iranian gardens, with selected examples: by means of a descriptive approach, based on documents, literature review, and library studies of the various stylistics and aesthetics of water in Iranian gardens.

3. Results and discussions

Veneration and sanctification of water: Water as symbol of purity in Iran has always been an omen of cleanliness and brightness and it was highly valued in ancient Persia. Respect and sainthood attributed to water are deeply rooted in Iran. Anahita, the goddess of water, has always been present in the Iranian beliefs and the invigorating water is divided into four parts in its origin to create a paradise in the heart of the desert [10].[1]

Source of water in Persian gardens: In most cases, Iranian garden ducts and natural springs have been the main sources of water supply in the gardens; the amount of water, its management and distribution done accurately and carefully have determined the garden's area. How to irrigate a garden – which is directly associated with the type of the land – is important wherever an Iranian garden is concerned.

Iran and the Iranians' interest in applying water in the garden is manifested in the fact that it has always been made to flow in different ways through the garden, enhancing its appeal and elegance [11].

[1] Anāhiti, also called Anāhitā: ancient Iranian goddess of royalty, war, and fertility; she is particularly associated with the last one. Possibly of Mesopotamian origin, her cult was made prominent by Artaxerxes II, and statues and temples were set up in her honour throughout the Persian Empire. In the Avesta, she is called Ardvī Sūrā Anāhitā ("Damp, Strong, and Untainted"); this seems to be an amalgam of two originally separate deities. In Greece, Anāhiti was identified with Athena and Artemis (Encyclopedia Britannica, 2010).

In dry and hot parts of Iran, where surface water could not be counted with, Iranian people tried extracting and flowing hidden water in the layers of the ground through to the subterranean channels. Qanats lead water from mountains to villages and fields. This system supplies underground water through a series of shafts that use gravity to bring water to the surface (Fig. 1).

Figure 1. Aerial view of a qanat passing underground, located near Yazd [7]

Water supply in Persian gardens: There are clear relationships between the geometry, the layout of the gardens, and water supplying networks. The water affects geometry and axial composition, which is the channel's network directed to the geometrical formation of the garden. There is a classification into four parts for the needs of a water supplying network that shows that the garden geometry is based on the layout of the gardens. The geometry is created by the water supplying system and the needs are caused by the logic of water which matches well with the water supplying networks [5]. The Iranian garden as a whole cannot be visualized without water. The more water is available, the greater the role it plays in the garden landscape design. When water resources are abundant, the main construction of the gardens is moved to the nearest water source [8].

In this case, we can refer to the Farahabad garden[2] in Isfahan and the Shah-Guli garden[3] in Tabriz – these are the good examples of pavilions located inside the pond.

[2] Isfahan's Farahabad Garden was considered one of the most important historic gardens of Iran, despite its short life. Construction of the garden began in 1697 AD. An island was created in the middle of the lake and to the north, beyond which there was a palace, a narrow path connecting the island to the garden.

[3] The Shah–Guli (Royal Basin), one of the few gardens still remaining in Tabriz, was built in 1785 or possibly earlier. Tabriz is the capital of East Azerbaijan province.

The main role of watering in the Persian garden: There are two main roles of watering in the Persian garden: functional and decorative.

Functional aspect of water: Irrigation is a major functional aspect of water in the Persian garden, and water used for cleaning purposes as well. Dividing the garden into a square or a rectangular shape, and using straight lines, make the irrigating of the garden easy – resulting in less wasted water and a timeless design that still works. Water from an aqueduct, a reservoir, or water-lifting device would enter the channels and be distributed through the quadrants. Water flooded each quadrant long enough for plant roots to be reached. Access was allowed or denied through opening or blocking entrance points with mud or stones.

Decorative aspect of water: The Persian garden features water for various decorative aspects, such as jets, fountains, pools, channels, and waterfalls, in order to get better water volume and symphonies. The qualities of water afford a range of opportunities in gardens. Pools that contain fish or ducks encourage plant growth, each of these elements contributing to a subtle movement of the water. Tanks or channels with fountains are eye-catching and lure the ears; besides spray action, the drops hitting the water surface provide pleasing sounds and rippling movements. The water's constantly changing behaviour offers contrast to the fixed elements of the garden: walls, footpaths, and statues. As water keeps moving, its circulation affects the air, cooling and moistening it. Playing in the sunlight, the falling water drops add a light-splitting dimension. The sound of falling or moving water alters other sounds, blocking or transforming them. Still water offers a distinct silence.

Directed water can produce particular effects, such as the plane that forms – horizontally or vertically –, when water is forced through specific-sized openings. Water can slide silently, fall noisily, tumble gracefully, or splat messily. Thus, the water's effect on the quality of the environment is inestimable [6].

Jets, fountains. Water jets had places in indoor and outdoor pools. They spout water vertically with the effect of constructing a fountain by natural pressure. For example, the Hazar Jarib garden in Isfahan, created in the Safavid period, is served by five hundred jets. Lead pipes fed the jets. When the fountains are located in the main basin, they are the symbol of natural springs with a show of dancing water and pleasant sounds. Technology helped in – such as the nozzle design invented to spray the water in a variety of patterns that cooled the air and emitted distinctive sounds. Fountains became fixtures of Persian gardens [3].

Pools. Pools carry great importance in Persian gardens. Not for drinking, this water is in reserve for watering the garden, also with a cooling purpose, mirroring and settling dust on walkways and terraces. Pools vary in size and shape. The typical shapes were rectangular, square, circular, octagonal, and lobed or cross, and sometimes the size of the pool is related to the location and height of the building. Deep pools tend to be straight-sided. Basins are shallow and the walls of the pool are dark to reflect the building properly. Therefore, the walls of a pool are covered

by granite or dark marbles. Pirnia, the father of Iranian traditional architecture, wrote that the pool wall is higher than the pool itself in Persian construction and a gutter is built in it in order for the extra water to escape [9]. This method was created by Persian architectures. Water overflows when the water source is entirely filled, resulting in an apparently endless pool, if viewed closely. The pools are typically situated along the garden's long axis; they sit at right angles to larger areas. We can say that reflection is one of the main features of a pool in the Persian garden as it creates a special visual effect on the water surface; when pools appeared within pavilions, they were there to reflect ornately decorated ceilings. Sky reflecting on still water surfaces brings light and an illusion of space and it is very shiny. For instance, the water views of the Dolat Abad garden[4] in Yazd and Chehelsoton Garden[5] in Isfahan are exactly along the main axis and their dimensions match those of the buildings to completely reflect the picture.

Channels. Water motion renders a garden transiency, a sense of novelty as well as freshness. Water originally flowed through Persian gardens in narrow and shallow channels; broad expanses of paving extended to both sides of the channel are covered by brick or stone. The evolution of design has enabled these channels to become wider, changing how water was used in the structure. Channels are used for irrigation and decorative roles, the zigzag or wave patterns decoration giving the illusion of water movement. Also, sin-e kabkis have marbles, which are carved and have some inscriptions on their surfaces (mostly their inscriptions resemble fish scales), and they are used where water flows through channels in or out of the basins and pools. A linear water channel plays an important role in arranging the garden space, and this straight channel line acts as a symbol of infinity in the garden. The fluidity–flux could be a semiological interpretation of the river/creek. It is constantly changing. It is never still and draws along, dissolving whatever it finds in its course. [1]

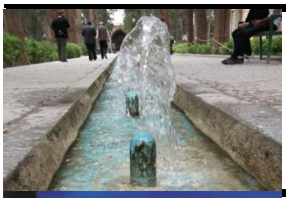
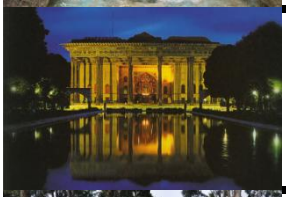
Waterfalls. In the main axes, water flows from one floor to the next floor when gardens are constructed on a slope. Iranians tried to use waterfalls to show the vertical surface of the water with the sound of water. By changing the levels at which water moved, they developed fountains capable of sending a directed cascade of water. The Shahzadeh Mahan garden[6] in Kerman is the most beautiful example of using steep slopes to make waterfalls.

[4] The Dolat Abad garden is located in the heart of the Iranian desert provinces of Yazd. It was built in the period of 1748–1799 and its design is one of the most unique and innovative of official Iranian gardens.

[5] The Chehelsoton garden is located in Isfahan Province; it was built in 1647, forming an approximate shape of a square; the main layout of the garden is along the three East–West axes.

[6] The Shahzadeh garden is located in a vast desert, on the slope of the Jupar Mountain, where water flows down to irrigate the agricultural land of the Qarieh Region of Mahan, the provinces of Kerman. The garden was built in ca. 1850 and was extended in ca. 1870.

Table 1. Aesthetic and functional aspect of water in the Persian gardens

WATER FEATURE	DENOMINATION	FUNCTIONAL AND AESTHETICAL ASPECT	GARDEN'S NAME
	**JET/ FOUNTAIN**	dynamism, action, movement, symbol of spring, sound effects	Hezar Jarib garden Fin garden
	**POOL/ BASIN**	compositional centre, turning point, reflection, water reservoir, static aspect	Eram garden Chehelsoton garden
	**CHANEL/ CREEK**	dynamism, linear compositional element, water transfer, irrigation, linkage and separation, visual axis	Fin garden, Shahzadeh Mahan garden, Dolat Abad garden
	**SINEH-E KABUKI**	perturbation, movement, wave making, showing more water in channel, sound effects	Chehelsoton garden Dolat Abad garden
	**CASCADE/ WATERFALL**	linkage and separation of different garden levels, visual axis, movement, sound effects	Shahzadeh Mahan garden Fin garden

4. Conclusion

Water, an archetypal symbolic element of life, was linked with numerous beliefs for the Persians, and thanks to its magical power it occupied a central place in the garden as well. Water in the Persian garden used decoration and irrigating systems, always opting for the simplest way, from a short distance so that a minimum of water is wasted. In accordance with the garden's geometrical shape, the water divided the garden into a square or rectangle so that people could irrigate easily. Water motion through channels, reflecting in pools, spraying from jets or

fountains, dripping or tinkling or lapping, presented functional and decorative elements in gardens – thus permeating them with meanings such as transiency, sense of novelty, or the concept of freshness with different temperatures inside the garden. The life-giving properties of the source, the fertile character of the garden that surrounds it and the cool feeling it emits, the water are personified by a goddess. Taking the arid Iranian climate into consideration, water sounds – rushing, sloshing, and splashing – make people feel like entering the paradise to hear different water sounds, colours, waves, and shapes.

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Abandonment phenomenon in Europe

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Abstract. In the last century, rapid transformations, industrialization, urbanization, tertiarization, the boom in services, modern counter-urbanization trends, social mobility, and bigger transport infrastructures could have been seen. The eastern Mediterranean area, located next to the Mediterranean Sea, was one of the most significantly changed parts of the agrarian lands in Europe. The recession left its mark everywhere in Europe. This paper focuses now on the land-use changes of the east coast of Spain, on the Huerta de Valencia. The objective of this paper is to assess spatial changes and to analyse the land-use changes between 2008 and 2013.

Keywords: land-use change, Mediterranean area, resilience, socio-ecological systems

1. Introduction

When considering agricultural landscapes, we refer to lands normally used for agricultural purposes and managed to provide adequate and durable production capacity [1]. Land abandonment is a phenomenon. It is applied to traditional lands or lands that have been used for agriculture but such activities on them have stopped for a while.

When we talk about abandonment, we have to clarify what it means exactly. It has a relative meaning. Baudry says there can be activity, but there is normally a change towards a less intensive pattern in the land concerned. It can be a land in itself, and there the soil stops being managed and used.

The phenomenon that is actually recognizable in the Mediterranean area refers to the last one. Traditionally, landscapes have changed.

They became intensively used systems, and spontaneous abandonment has started and changed the dynamics of them.

Mediterranean agricultural landscapes are specific cultural landscapes, resulting from a long history of human management adapted to restrictive environmental conditions and biological diversity [2]. They optimize the annual fluctuations in productivity without causing ecological degradations [3]. In the Mediterranean area, the abandonment reached a large proportion in the socio-economic system and in landscapes as well.

What is the process of land abandonment? It can take place by the death of agricultural activity, or the unsuccess of farmers. The process can be progressive. If there was cultivation, even if only for a certain period, it has been suspended; grazing becomes more extensive by less care concerning the pastures or reductions in livestock density; permanent crops are not maintained or improved by regular management measures even if they are still being exploited.

Naveh and Lieberman say the first step can also be the intensification of traditional use that has happened in the south part of the Mediterranean area. The extensive systems have changed to intensive, but the landscape was not able to totally adapt to the process. The Huerta de Valencia is defined as an agricultural plane irrigated by the River Turia. It surrounds Valencia and the east coast of Spain. Its origins are dated to the 8th century with the arrival of the Muslims. The Valencia Metropolitan area is the economic and administrative centre of the Valencian Region. The Huerta de Valencia connects three landscapes: the Turia River Natural Park with its riparian forests, the Albufera Natural Park, and the Mediterranean Sea.

The Huerta of the City of Valencia became a unique and interconnected landscape.

The values of Huerta are the main elements of its character. It has a historical structure with a dense network of channels, rural roads, and traditional buildings, like *barracas*. It has a strong agricultural activity, which changed the landscape.

Finally, it is irrigated by the Tribunal de las Aguas, the oldest active jury in Europe. It is a harmonious landscape which produces a patchwork of land uses and has a high visual value. Besides its visual and productive value, it creates the social memory of the locals. The Huerta de Valencia has been threatened by different factors throughout the centuries.

The main problem is the lack of co-ordination among the 45 involved municipalities, the fragmentation by the development processes, and the rising number of abandoned fields. These factors cumulatively cause the disappearance of the Huerta landscape.

In the last decade, the resilience theory has extended from the pure ecological domain – considering resilience as a property of ecological systems – to cultural landscapes (socio-ecological systems) [4].

The concept of resilience refers to the capacity of a system to experience shocks while retraining the same function, structure, and identity. It is the ability of dealing with disturbances or changes without altering the essential characteristics of the system [5].

The area of the Huerta de Valencia can be considered as a resilient landscape. It is the result of a long-lasting human interaction with the physical environment.

The Huerta is the most resilient landscape of its type. The Dobris report in 1998 emphasized that there are only six huerta landscapes left in Europe [6].

Despite the cultural representation of the Huerta – it is usually associated with horticultural crops –, different crops have been grown, adapting to the population needs in each historical period [7]. During the Middle Ages, lands were dominated by wheat and vineyard with olive and fruit trees on the edges, and vegetables were in small plots, while a mulberry tree forest covered the Huerta by the sixteenth century. In the nineteenth century, horticultural crops became the dominant vegetation; and it was not until the second half of the twentieth century that citric trees started to expand [8].

At the beginning of the twenty-first century, the Huerta de Valencia, like other traditional landscapes [9], experienced unprecedentedly fast and profound changes. Now, due to the economic crisis, there has been a lack of infrastructure growth. The problems related to the low profitability of agriculture persist as well as the threat of abandonment.

This work refers to the analysis done during 2014 and 2015 at the Department of Rural Engineering, Technical University of Valencia, and supervised by Prof. María Vallés Planells.

2. Materials and methods

The study analyses an 11,370-ha area. It composes twenty-four units delineated for Huerta de Valencia Action Plan. The starting point of the work was the land-use map developed in 2008, in which land use corresponds to land cover. It means that it refers rather to natural or human-introduced elements that cover the surface. The identification of land use in 2013 was performed with the aid of ArcGIS software. For this task, the latest available aerial photograph – which corresponded with the 2012 flight – was used. A new class "infrastructure," which was classified as "urban processed areas" in 2008, was included during this stage. These new infrastructures were mainly connected to the CV-300 road in the north and the high-speed railway in the south (AVE). Finally, the field survey was developed during May 2014. It was conducted on a set of sample areas that were based on buffer areas of 500 meters around a set of randomly selected points that were spatially distributed among the 24 landscape units (*Figure 1*). As a whole, the sampled area was of 1,806 ha, which involved 16% of the study area.

The detection of abandonment was not straightforward. The edge between abandonment and agricultural use may not be sharp enough because abandonment may occur at different degrees of intensity. Here, abandonment includes fields that have lost their regular characteristic pattern of cultivation because agricultural use has completely stopped or management intensity has become very low.

The map classifies 17 types of land uses divided into two main groups: vegetated and non-vegetated surfaces. The vegetated surface applies to areas that have a vegetated cover of at least 4% for at least two months of the year; they are cultivated or contain natural vegetation. These covers consist of the life forms.

Artificial surfaces describe areas that have artificial cover because of human activities with less than 4% vegetative cover.

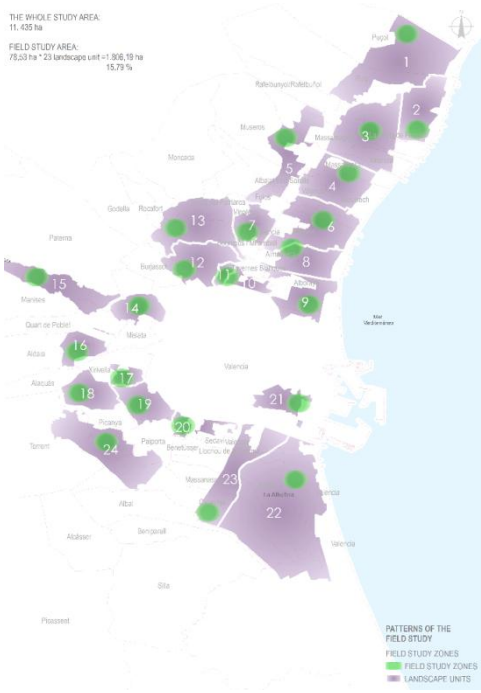

Figure 1. Distribution of sample areas

3. Results and discussions

The analysis of land-use change in the Huerta de Valencia as a whole shows three main dynamics during the period between 2008 and 2013. First, results show that there has been a decrease in the area covered by citrus from 32.2% to 24.8%, which corresponds to a decline of 23% in citrus as compared to 2008. According to

cross-tabulation, 15% of the area covered by citric fields in 2008 has become abandoned and 9% has been converted into irrigated arable land in 2013. Second, the percentage of abandonment or of the fields in bad condition has increased from 11.1% to 15.6%, which involves a rise of 40.8% as compared to 2008. Cross-tabulation shows that the surface increase of abandonment is mainly through citrus (31%) and irrigated arable land (9.6%). Finally, the emergence of recently cultivated fields is also remarkable (4% of the total area in 2013). According to the data derived from the fieldwork, most of these newly cultivated areas would correspond to horticultural fields (97%) and 3% would correspond to other fruit trees, especially khaki fields. This fact would involve that the area of horticultural fields has not decreased, but there has been a slight increase of 6.2% in the area covered by irrigated arable land as compared to 2008 (*Figure 2*).

Concerning the analysis of change with regard to the land-use values in 2008, results also show a marked rise in palms (53.5%) and asphalted fields (22.4%). However, they are not considered significant since they occupy less than 1% of the total area. There is also a drop in urban processed areas (13.8%) which are mainly connected with the new high-speed railway (AVE) and CV-300 road. The artificial surface (containers, industry, installation, urban processed areas, infrastructure, store and asphalted field, and landfill) has not significantly increased. It has risen from 4.7% to 5.4%. This increase is mainly due to the new infrastructures and areas in urban process.

Table 1. Cross-tabulation for land-use change in the period of 2008–2013 in the Huerta

	LAND USE 2008															
LAND USE 2013	Rice	Citrical	Containers	Horticultural	Industry	Installation	Greenhouse	Wetland	Urban process	Palms	Abandoned field	Storage field	Asphalted field	Landfill	Nursery	TOTAL 2013
Rice	1790,5										0,2					1790,8
Citrical		2760,4		34,3			0,2				22,7				0,2	2817,8
Containers			20,8													20,8
Horticultural	0,9	322,7		3457,6			0,3			1,0	146,2			0,4	5,6	3934,7
Industry		0,6		1,7	182,1						4,4			0,1	0,3	189,3
Installation				0,6		119,6			0,3		0,2					120,7
Greenhouse				8,7			67,3									75,9
Wetland				5,6				204,0		0,4	11,6	0,1				221,6
Urban process		5,6		5,6			0,1	1,6	60,5		34,1	0,3		0,4	4,0	112,3
Infrastructure		7,2		10,8	0,0				65,6		5,5			1,1	0,4	90,6
Palms		5,2		4,0						7,7	2,0				0,8	19,7
Abandoned field	0,6	550,0		171,2	0,4		2,5		3,7	3,7	1035,5	0,5		0,4	9,5	1778,1
Storage field		0,1		0,3							0,2	33,0				33,5
Asphalted field		0,4											2,0			2,4
Landfill														46,8		46,8
Nursery		3,8		3,5											103,1	110,4
Other fruit trees		4,0		2,2							0,4					6,7
TOTAL 2008	1792,1	3660,1	20,8	3706,0	182,6	119,6	70,4	205,6	130,3	12,8	1263,0	33,9	2,0	49,2	123,8	11372,2

Figure 2. Examples of newly cultivated areas in the Horta de Faitanar (19), Horta de Picanya (24), and Horta de Campanar (14) between 2008 and 2013

When analysing land-use evolution unit by unit, results show different patterns of land-use changes (*Figure 3*) as follows:

Unit 22 (Horta de la Séquia de L´Or I Arrossars de L´Albufera). It is part of Albufera Natural Park and rice is the dominant form of land use. Abandonment is scarce.

Units 6, 8, 9, 10, 11, and 12 (Horta de Meliana, Hortad´Almàssera I Alboraia, Hortad´Alboraia, Horta de San Miquel del Reis, Horta de Petra, Horta de Poble Nou).

They are dominantly irrigated arable lands (this land use covers more than 70% of the units) and with some scattered abandoned fields that involve less than 6% of the units.

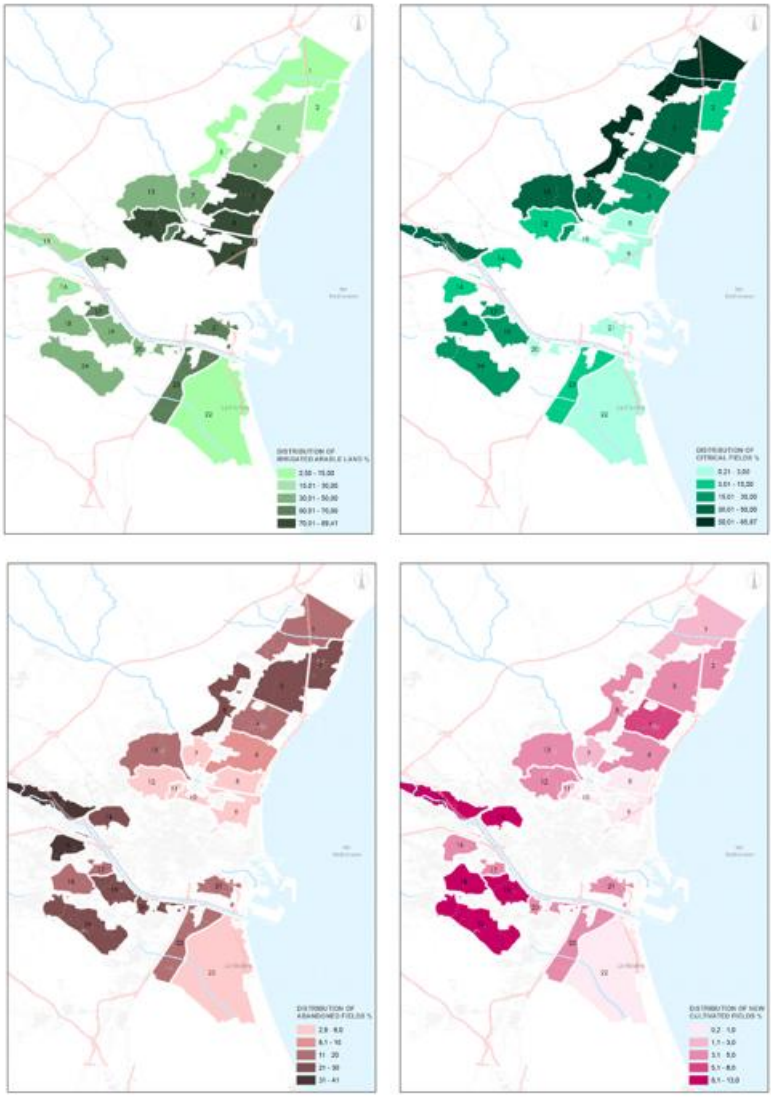

Figure 3. Percentage of irrigated arable land, citrus, abandonment, and new cultivated areas in 2013 within the different units that compose the Huerta de Valencia

Newly cultivated areas are not significant except for units 6 and 12 (Horta de Meliana, Horta de Poble Nou) which correspond to 3% of the units.

Units 7 and 13 (Horta de Vinalesa, Bonrepós I Mirambell, Horta de L´Arc de Moncada). Both units show a mosaic mainly composed by horticultural and mosaic fields with some recent khaki crops. With regard to the level of abandonment, there has been an increase from 6% to 16% in unit 13 as compared to unit 7, which has 5% abandonment in 2013. Newly cultivated areas, including khaki, involve between 2% and 4% of the unit.

4. Conclusions

According to the results, 13% of the analysed territory has changed. The main changes are the decrease in the area covered by citric fields (7.4%), the increase of abandonment or of areas in bad condition (4.5%), and the increase of irrigated arable lands (2%). The latter, being one of the most significant changes, is through the conversion of citric and abandoned fields. As a whole, the loss of cultivated land in the Huerta de Valencia is similar (6.5%) to the average value for the Valencian Region (6.3%). However, results indicate that land-use dynamics are not homogeneous within the Huerta de Valencia. The increase of abandonment goes from 1% in the most stable units to 13% in the most degraded ones. The work shows a simple methodology to show how we can analyse changes in land use between such short periods of time and get some ideas about a resilient landscape.

Acknowledgements

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Elemental profile of edible mushrooms from a forest near a major Romanian city

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Abstract. We determined the elemental profile of 16 edible mushroom species from the Făget Forest, near Cluj-Napoca, and of 12 species from the Apuseni Mountains. One-way ANOVA showed no difference in the elemental content of mushrooms when the two regions were compared. Some species accumulated high amounts of trace elements, i.e. *Boletus edulis* (Ag, S, Zn), *Macrolepiota procera* (Cu), *Lactarius volemus* (Co), *Russula emetica* (Mn), *Armillariella mellea*, and *Chantarellus cibarius* (Cr). The cadmium content was the highest in the case of *Leccinum scabrum* and *Boletus edulis*. These two species presented elevated risk levels for all age-groups when they are consumed regularly.

Keywords: wild edible mushrooms, heavy metals, ICP-OES, trace elements

1. Introduction

The consumption of wild grown edible mushrooms is a worldwide custom. In Transylvania (Romania), there is a strong tradition of collecting wild edible fungi for eating and selling. Edibility assumes the absence of poisonous effects, a pleasant taste and aroma, and nevertheless the lack of concentrations of accumulated toxic elements dangerous to human health. However, this last aspect is often ignored by the collectors. Edible mushrooms constitute an important and widely appreciated part of the human nutrition because they are rich sources of

proteins, fibres, vitamins, antioxidants, and minerals. Some elements are essential for living organisms, including chromium, cobalt, copper, iron, manganese, and zinc. Wild edible mushrooms constitute one of the main sources of these elements [1]. In the last few decades, the mapping of elemental content of mushrooms was at the centre of many chemical researches. These studies revealed specific elemental preferences of some mushrooms. For example, *Macrolepiota procera* accumulates mainly copper, but it can contain high amounts of Mn, Zn, Cr, Ni, even Cd [2–5]; *Chantarellus cibarius* shows preference for Mn, Fe [6]; *Boletus edulis* is known for its high content of Se, Ag, Mn, and Zn [2, 5, 7] and *Armillariella mellea* for iron [2, 8]. There are also some species, which are known for their low mineral content (*Lactarius spp*., *Russula spp*., *Hypholoma fasciculare*, *Hydnum repandum*) [2, 4, 7, 9–14]. Relying on several studies, a review paper highlighted the uneven distribution of the elements in the fruiting body of the mushrooms: the highest concentrations of metals can be found in the sporophore, followed by the other parts of the cap. The smallest metal content is found in the stipe [7].

Today it is also known the ability of some mushroom species to accumulate considerable amounts of metals as well as toxic elements with regard to the human organism, such as mercury, cadmium, lead, arsenic, or radionuclides [7, 15–19]. Near highly contaminated sites (smelters, metal mining, thermal power plants, industrial areas) and main roads, high content of heavy metals was detected in mature fruiting bodies of macrofungi [8, 9, 20–22]. A recent study on mushrooms growing in urban areas showed unusually elevated concentrations of Cd and Pb in the fruiting bodies [23].

These findings led us to hypothesize that a large city as Cluj-Napoca may have polluting effect over the mushrooms growing in the forest lying in the close vicinity of it. The city is the economic and cultural centre of Transylvania; in the last few years it has developed rapidly. With its increased road and air traffic and its expanding trends, it may pollute the Făget Forest, which is situated on the western and southern side of the city. Many inhabitants of Cluj-Napoca have the habit of going mushroom picking in the Făget for consumption purposes. The most popular species are *Lactarius piperatus*, *Boletus edulis*, *Armillariella mellea*, *Macrolepiota procera*, *Russula spp.*, and *Agaricus spp*.

Our aim in this study was to determine the elemental composition of mushrooms growing in the Făget Forest, and thus to assess the health risk arisen from the long-term consumption of them. We also established the background levels of the elements in mushrooms by choosing an area considered unpolluted in the Apuseni Natural Park.

2. Materials and methods

Description of the sampling sites

The Făget Forest is part of the Făgetul Clujului – Valea Morii Natura 2000 Network (ROSCI0074). It lies at an average altitude of 625 m and it consists dominantly of beech, less hornbeam, and spruce. The prevailing wind direction is from the west, the average annual temperature is 8.4°C, and the average annual precipitation is 663 mm [24]. The control site consisted of the surroundings of Padiș, at an average altitude of 1,127 m, situated in the Apuseni Natural Park, also part of the Natura 2000 Network (ROSCI 0002). The average annual temperature is 6.0°C and the average annual precipitation is 1,400 mm [24]. This site is covered with pinewoods; the dominant species is the *Picea abies*. In order to collect mushroom species whose habitat is the deciduous forest, we chose the beech forests at lower altitudes but close to Padiș.

Sampling and sample proceeding

A total number of 80 mushrooms of 16 species were collected from the Făget Forest and 60 mushrooms of 12 species from the Apuseni Natural Park in July–October 2014. At least three individuals were picked up of the large-size species and at most 7 individuals of the small-size species. The samples were stored in plastic bags. The mushrooms were cleaned with tap water, and rinsed with distilled water. Further on, the caps and stipes were processed separately. They were dried at room temperature, and air-dried at 105°C. The mashed and sieved powders, having the particle diameters less than 315 μm, were stored in plastic bottles until the digestion process. For the instrumental analysis, three samples were digested in parallel for each part (caps and stipes) of any mushroom species. The decomposition of organic matter was carried out at atmospheric pressure, using a digestion mixture of 5 mL 65% HNO_3 (Merck, suprapur) and 4 mL 30% H_2O_2 (Merck, suprapur). The solution of nitric acid was added at room temperature to a mass of 0.2000 g sample, twelve hours prior to the heating process. The digestion was done at 90°C for 4 hours on an electric heating plate. The hydrogen-peroxide solution was added in two steps. The resulting digests were analysed with Agilent 5100 ICP-OES spectrometer, applying the simultaneous measuring technique. The calibration was performed with multi-elemental standards, and calibration curves were obtained for each element. A total of 20 elements (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, S, Si, Sr, Zn) were quantified.

Method of the risk assessment

The risk assessment of the heavy metals to human health due to the consumption of the mushrooms can be evaluated by calculating the hazard quotient

(HQ) for each metal of interest and the hazard index (HI), which is the sum of the hazard quotients [25, 26]. The HQ is the ratio between the exposure and the reference dose (*Eq. 1*). One can assume the existence of a risk for mushroom consumption when the HQ > 1.

$$HQ_{metal} = \frac{DI \cdot C_{metal}}{R_f D \cdot BW} \quad (1)$$

where DI is the daily intake of mushrooms (kg day^{-1}), C_{metal} is the concentration of the metal in the mushroom given for dry weight (mg kg^{-1}), R_fD is the oral reference dose for the metal given for unit body weight (mg kg^{-1} day^{-1}), BW is the average human body weight (kg). We used the R_fD values published in the IRIS (Integrated Risk Information System) database, and they can be seen in *Table 1* [27]. We used average body weights for different age-groups as reported by the guidance of the European Food Safety Authority [28]. The age-groups and BW values are given in *Table 3*.

The HI provides information about the joint health risk caused by the heavy metals when a specific mushroom is consumed. We calculated the hazard index as given by *Eq. 2*.

$$HI = HQ_{Cd} + HQ_{Cr} + HQ_{Mn} + HQ_{Ni} + HQ_{Zn} \quad (2)$$

Statistical analysis

The statistical analyses were performed with R software (version 3.2.1, R Foundation for Statistical Computing) and Past software. We created a data matrix where the rows represented the caps and stipes of the mushroom species collected from the Făget Forest, while the columns contained the concentrations of the 20 studied elements. Before the statistical analysis, the concentration data were standardized, that is transforming the distributions of the variables in order to achieve distributions with zero means and standard deviations of 1.0. Thus, the differences in the concentration of major and minor elements, which were as huge as 4–6 orders of magnitude, were equilibrated. We studied the correlation between the elements with the Spearman rank correlation test. In order to compare the elemental composition of mushrooms grown in the selected geographical regions and the elemental distribution in the caps and stipes, we performed one-way ANOVA. Prior to the analysis, outliers were identified by Dixon Q-test for each element, and excluded from the dataset.

3. Results and discussion

The concentration means (n = 3) for the elements quantified in the mushrooms from the Făget Forest are shown in *Table 1* and *Table 2*. The *Boletus edulis*

accumulated high amounts of Ag, S, and Zn; the *Macrolepiota procera* accumulated Cu; *Lactarius volemus* had the most elevated concentration of Co; *Russula emetica* preferred Mn; *Armillariella mellea* and *Chantarellus cibarius* accumulated Cr. The cadmium content was the highest in the case of the *Leccinum scabrum* and *Boletus edulis*. The *Lactarius deliciosus*, *Lactarius volemus,* and *Amanita rubescens* species had the lowest mineral content.

The one-way ANOVA test revealed no significant differences between the elemental compositions of the mushrooms coming from the two selected areas. An exception was the Ba, which had significantly ($p = 0.035$, Fisher's $F = 4.92$, $df = 28$) higher concentrations in the mushrooms from Făget than in the Apuseni Mountains. We also compared the elemental composition of caps and stipes of the 16 mushroom species using one-way ANOVA. Relying on the Fisher's F values, the Ca, Cr, Li, Ni, and Zn concentrations were significantly ($p < 0.05$) higher in the caps than in the stipes of the fungi.

According to the Spearman rank correlation test (*Table 4*) carried out based on the concentrations of elements present in the mushroom caps and stipes from the Făget Forest, we found significant ($p < 0.05$) correlation between the alkaline-earth metals (Ca-Sr, Ba-Sr, Ba-Ca), where rho was higher than 0.60. A strong correlation was also between the Mn with Ca, Ba, Sr, and P (rho > 0.70). Magnesium was not correlated with these elements, but it had rho values between 0.41 and 0.53 with transitional metals such as Ag, Cd, Cu, and Fe. An interesting finding was the significant inverse correlation of sulphur with Ca, Ba, Sr, and Mn, and stronger positive correlation with Ag, Cd, Zn, and P. We also found significant correlations between other pairs of elements such as Fe-Mn, Fe-Cr, Fe-Na, K-Na, K-Al, Fe-Al, Cd-Zn, Cd-Ag, and Cu-Mg. Other studies on mushrooms found the same correlations between elements [4, 29].

In order to assess the contribution of some heavy metals to the health risk of mushroom consumption, we calculated the hazard quotients. The highest hazard quotient values were found for Cd (0.034–2.216), followed by Zn (0.014–0.201), but Cr (0.00001–0.00026) showed the lowest values. We evaluated the health risk of mushroom consumption concerning different age-groups relying on the hazard index (*Table 3*). Assuming that the mushroom season lasts 6 months (from May until October), in the calculus we reckoned with a weekly mushroom consumption of 1 kg (DI = 0.143 kg day^{-1} fresh weight) for adults and adolescents beyond 14, and of 0.5 kg (DI = 0.071 kg day^{-1} fresh weight) for children and teenagers. The average water content of the mushroom fruiting body was considered as 90% [2].

Table 1. The concentrations (mg kg^{-1}, dry weight) of alkaline, alkaline-earth metals and non-metals in the mushrooms from the Făget Forest

Mushroom species	Parts	K	Na	Li	Ca	Mg	Ba	Sr	P	S	Si
Agaricus campestris	cap	27049	83.32	0.21	68.85	1065.1	2.53	0.55	10107	4886	81.83
	stipe	29924	102.28	0.25	158.96	645.5	1.04	0.62	5954	4418	121.60
Amanita rubescens	cap	60512	509.09	0.21	445.12	1311.6	2.20	0.75	10234	8612	25.87
	stipe	41674	580.04	0.25	277.59	492.3	1.08	0.50	5013	5998	15.36
Amillariella mellea	cap	44370	441.56	0.21	836.68	1078.1	1.79	0.96	6506	1925	38.94
	stipe	48270	428.33	0.02	703.69	699.8	6.36	1.50	1574	668	80.26
Boletus edulis	cap	33814	163.19	0.05	334.83	819.4	0.42	0.33	7821	17378	30.88
	stipe	25441	115.37	0.02	237.04	585.8	0.62	0.25	5052	16867	32.46
Chantarellus cibarius	cap	33815	151.63	0.17	481.59	968.4	1.87	1.08	3676	868	49.95
	stipe	34654	139.07	0.54	576.72	516.7	2.75	1.46	2060	488	35.97
Hydnum repandum	cap	46990	404.80	0.02	235.09	1115.8	1.96	0.50	7808	1913	45.35
	stipe	40230	380.31	0.38	481.65	788.3	5.24	0.96	5901	1426	24.28
Hypholoma fasciculare	cap	29577	317.49	0.37	448.35	947.7	1.37	0.67	6716	1943	27.97
	stipe	23506	194.70	0.17	328.75	421.4	2.04	0.79	2936	1023	59.97
Lactarius deliciosus	cap	21312	77.30	0.02	231.48	889.7	0.58	0.62	4265	1587	45.56
	stipe	15049	115.02	0.05	310.43	485.8	1.44	0.96	2407	1061	23.40
Lactarius piperatus	cap	33823	172.81	0.25	248.26	802.5	1.12	0.37	4833	5479	48.37
	stipe	43218	245.02	0.42	193.42	459.4	0.87	0.33	2529	3493	38.33
Lactarius volemus	cap	25340	161.61	0.09	296.08	612.7	1.67	0.62	3626	1495	71.03
	stipe	23430	209.87	0.26	294.78	373.8	1.25	0.58	1905	1136	61.65
Leccinum scabrum	cap	37567	295.93	0.26	387.18	825.2	1.83	0.62	5704	3891	32.09
	stipe	33132	202.61	0.14	417.59	313.1	5.11	0.87	2301	1717	59.23
Macrolepiota procera	cap	31953	137.69	0.42	137.18	1250.0	1.87	0.33	12461	5301	28.18
	stipe	38198	475.30	0.02	649.49	972.9	5.56	2.16	9545	5683	69.17
Russula alutacea	cap	36915	207.33	0.02	275.99	781.4	2.66	0.75	4819	2162	31.79
	stipe	27366	494.47	0.50	129.89	364.6	0.79	0.25	2146	1167	41.70
Russula emetica	cap	37968	284.18	0.17	601.78	868.1	5.69	1.33	4324	1356	49.65
	stipe	21798	248.88	0.53	793.20	810.9	6.68	1.47	6752	1698	49.97
Russula virescens	cap	40459	155.27	0.14	200.09	1030.4	0.87	0.42	5956	4007	24.69
	stipe	42346	210.27	0.66	327.66	547.2	1.33	0.66	3241	2001	36.86
Tricholoma portentosum	cap	32438	262.65	0.62	378.45	1104.7	1.25	0.58	12068	2993	37.12
	stipe	26396	377.16	0.25	963.06	531.41	3.57	1.79	2413	933	46.39

Table 2. The concentrations (mg kg^{-1}, dry weight) of minor and trace elements in the mushrooms from the Făget Forest

Mushroom species	Parts	Ag	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
Agaricus campestris	cap	2.82	23.74	0.76	0.24	0.439	64.01	88.47	8.2	0.33	115.56
	stipe	11.76	52.13	0.61	0.18	0.548	73.79	80.22	10.1	0.34	60.61
Amanita rubescens	cap	0.50	115.76	0.91	0.25	0.166	41.48	101.77	26.5	0.75	137.89
	stipe	0.11	55.50	0.50	0.37	0.075	18.85	44.43	9.8	0.67	78.51
Amillariella mellea	cap	0.54	112.92	2.96	0.12	1.915	14.95	102.27	26.5	0.50	57.38
	stipe	0.37	198.61	0.71	0.12	0.416	7.89	208.28	63.1	0.25	20.15
Boletus edulis	cap	14.61	14.69	4.62	0.25	0.075	30.58	50.06	8.7	0.62	163.21
	stipe	7.86	10.39	2.58	0.25	0.075	17.71	38.48	6.6	0.33	89.11
Chantarellus cibarius	cap	0.37	70.44	0.50	0.12	1.704	45.92	94.75	16.1	0.33	69.15
	stipe	0.12	36.93	0.17	0.12	1.831	20.69	35.26	19.5	0.79	34.05
Hydnum repandum	cap	0.58	133.72	0.62	0.12	0.375	35.32	218.26	23.7	0.25	52.43
	stipe	1.71	53.99	0.29	0.12	0.191	31.03	86.95	54.0	5.23	39.80
Hypholoma fasciculare	cap	5.54	26.14	1.00	0.12	0.075	32.59	128.13	19.9	0.25	64.15
	stipe	3.71	35.69	0.37	0.12	0.075	18.45	84.71	29.1	0.25	38.94
Lactarius deliciosus	cap	0.25	52.41	1.62	0.12	0.091	7.44	80.17	4.4	0.25	70.77
	stipe	0.12	31.32	0.75	0.12	0.075	8.23	32.97	3.7	0.37	56.72
Lactarius piperatus	cap	6.03	34.01	2.70	0.29	0.091	64.47	52.55	8.3	0.29	116.44
	stipe	1.21	21.32	0.87	0.75	0.191	38.54	29.89	4.3	0.25	71.08
Lactarius volemus	cap	0.42	25.35	0.87	8.78	0.125	65.15	37.43	22.8	2.29	61.12
	stipe	0.22	53.67	0.33	5.32	0.150	40.21	58.16	15.0	1.00	42.79
Leccinum scabrum	cap	0.46	46.60	10.85	0.12	0.091	27.89	85.63	27.2	0.25	110.70
	stipe	0.12	60.23	4.36	0.12	0.075	11.59	46.27	44.0	0.37	47.85
Macrolepiota procera	cap	7.78	40.84	2.54	0.12	0.192	147.30	76.06	13.4	0.25	74.15
	stipe	6.64	137.71	1.41	0.29	0.091	148.04	96.40	24.2	0.25	67.67
Russula alutacea	cap	0.66	37.78	1.41	0.12	0.075	36.66	76.27	23.5	0.83	85.56
	stipe	0.11	24.30	0.37	0.50	0.075	22.38	92.94	10.0	0.75	295.22
Russula emetica	cap	1.12	22.97	1.12	0.25	0.075	38.63	56.46	67.0	0.25	83.42
	stipe	4.11	57.73	0.51	0.14	0.217	44.43	90.10	82.0	7.93	46.55
Russula virescens	cap	0.46	65.94	0.87	0.81	0.091	42.01	45.41	14.5	6.27	94.40
	stipe	0.25	98.64	0.25	0.50	0.150	23.93	47.39	13.0	2.16	74.78
Tricholoma portentosum	cap	4.28	43.13	1.71	0.12	0.075	64.77	73.71	19.1	0.37	81.20
	stipe	0.21	25.98	0.46	0.17	0.075	30.59	50.17	44.2	4.07	65.38

For adults and adolescents, only two species, the *Boletus edulis* and *Leccinum scabrum*, pose a health risk when the mushroom is regularly consumed. Children under 10 years of age and toddlers are exposed to a greater degree with regard to several species. The mushrooms with the highest risk levels were the *Boletus edulis*, *Leccinum scabrum*, *Russulacea spp*., *Lactarius spp*., and *Armillariella mellea*. However, the mushrooms with the lowest HI values were: *Chantarellus cibarius*, *Hydnum repandum*, *Agaricus campestris*, and *Lactarius volemus*.

Table 3. The hazard index values for the caps of mushrooms grown in the Făget Forest

Hazard index (HI)					
Age-groups	1–3	3–10	10–14	14–18	adult
Average body weight (kg)[#]	12	23	43	61	70
Agaricus campestris	0.72	0.38	0.20	0.29	0.25
Amanita rubescens	0.95	0.49	0.26	0.38	0.33
Armillariella mellea	1.99*	1.04*	0.56	0.79	0.69
Boletus edulis	3.11*	1.62*	0.87	1.23*	1.07*
Chantarellus cibarius	0.51	0.27	0.14	0.20	0.18
Hydnum repandum	0.58	0.30	0.16	0.23	0.20
Hypholoma fasciculare	0.81	0.42	0.23	0.32	0.28
Lactarius deliciosus	1.12*	0.59	0.31	0.45	0.39
Lactarius piperatus	1.87*	0.98	0.52	0.74	0.65
Lactarius volemus	0.80	0.42	0.22	0.32	0.28
Leccinum scabrum	6.76*	3,53*	1.89*	2.68*	2.33*
Macrolepiota procera	1.71*	0.89	0.48	0.68	0.59
Russula alutacea	1.13*	0.59	0.31	0.45	0.39
Russula emetic	1.12*	0.58	0.31	0.44	0.39
Russula virescens	0.95	0.50	0.26	0.38	0.33
Tricholoma portentosum	1.26*	0.66	0.35	0.50	0.44

[#]**Source: European Food Safety Authority Journal [24]**

4. Conclusions

The comparative study of the wild edible mushrooms from the Făget Forest and the Apuseni Mountains showed no significant differences in the concentration of 19 macro-, micro-, and trace elements. Only barium was significantly higher in the mushrooms grown in the Făget. The hazard index values were relatively low. Two species (*Boletus edulis* and *Leccinum scabrum*) may be considered to have slightly elevated risk levels when they are consumed regularly. The element with the highest contribution to the hazard index was the Cd. However, other studies revealed the cadmium-accumulating capacity of these species [2, 6]. We can conclude that the polluting effect of Cluj-Napoca as a city with high traffic and continuous expanding trends was not detectable in the wild-growing mushrooms.

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Identification of new superwarfarin-type rodenticides by structural similarity. The docking of ligands on the vitamin K epoxide reductase enzyme's active site

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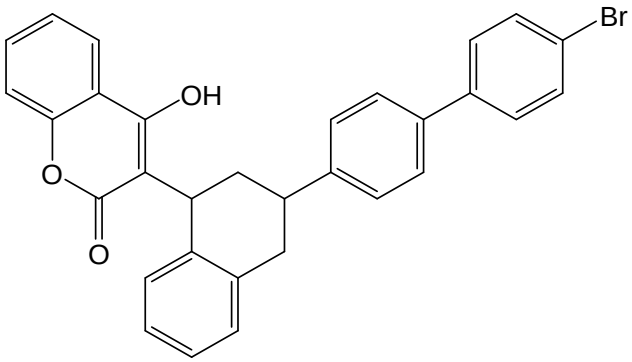
Abstract: The rodenticide brodifacoum is highly toxic to mammals and birds, and extremely toxic to fish. It is a highly cumulative poison due to its high lipophilicity and extremely slow elimination. For this reason, it may be interesting to find similar compounds in order to enlarge the spectrum of vitamin K epoxide reductase enzyme inhibitors used today in pest control. We used the Similar Compounds search type of the Chemical Structure Search of the PubChem Compound Database to locate records that are similar to the chemical structure of brodifacoum, using pre-specified similarity thresholds. Using the threshold ≥ than 95% for the similar structures criteria, we found 14 compounds (from over 30 million entries) that meet this criteria. Two of these compounds have a better binding affinity to vitamin K epoxide reductase enzyme than brodifacoum, but the binding energy of the other 12 substances is also high, having identical or lower lipophilicity; consequently, they will eliminate faster, possibly lacking a part of the adverse effects.

Keywords: brodifacoum, structural similarity, screening, docking

1. Introduction

Brodifacoum (PubChem Compound Identifier, CID=54680676) is a coumarin-derived rodenticide. It was first introduced in 1975 to deal with the public health problem of warfarin-resistant rodents.

Brodifacoum is a weak acid which does not readily form water soluble salts. It does not lose activity after 30 days in direct sunlight. This rodenticide is effective against warfarin-resistant rats. Currently, it is registered for the control of rats and mice in and around farm structures, households, and domestic dwellings, inside transport vehicles, commercial transportation facilities, industrial areas, sewage systems, aircraft, ships, boats, railway cars, and food processing, handling, and storage areas. Products containing brodifacoum are available to the general public and application may be made as often as necessary. Brodifacoum is formulated as meal bait, paraffinized pellets, rat and mouse bait ready-to-use place packs, and paraffin blocks. All end-use products contain 0.005 percent active ingredient. [1]



54680676

Brodifacoum was made a "restricted-use" pesticide in 2008 by EPA, meaning it can only be used by certified pesticide applicators. The product remains on the market for public use.

Brodifacoum is absorbed through the gut and works by preventing the normal clotting of blood, leading to fatal hemorrhage [1]. It inhibits coagulation by antagonizing the action of vitamin K. Warfarin prevents the recycling of vitamin K by blocking vitamin K epoxide reductase (VKOR) activity, thus creating a functional vitamin K deficiency. Inadequate gamma-carboxylation of vitamin K-dependent coagulation proteins interferes with the coagulation cascade, which inhibits blood clot formation. [2]

Death usually occurs through gastric hemorrhage. It is retained in the tissues at high rates, sometimes remaining in organ systems during the entire lifetime of an exposed animal. In a study that measured the retention of radioactive brodifacoum in the livers of single-dosed rats, 34% of the single dose is found in the liver after 13 weeks, and 11% of the dose remained in the liver for 104 weeks, approaching the normal lifespan of a rat. [1]

It is highly effective in small doses – usually a rodent ingests a fatal dose after a single feeding and will die within 4-5 days. The greatest risk to wildlife from brodifacoum is secondary poisoning. Rodents continue to eat poisoned bait, so at the time of death the amount of brodifacoum present in their bodies is many times the amount required to kill them. Non-target wildlife, such as predators and scavengers, may then consume rodents that have ingested large doses of brodifacoum [1]. It can take as little as one poisoned rodent, or a predator may accumulate enough brodifacoum after consuming several poisoned prey items, to induce life-threatening or fatal effects. A single dose of brodifacoum can depress blood clotting for months in some animals, including birds. Stress or slight wounds incurred in the field, such as small scratches that normally occur when a raptorial bird captures its prey, are often sufficient to cause a fatal hemorrhage [1].

It is very highly toxic to aquatic organisms, mammals and birds. Due to its extremely low solubility and usage patterns, however, it is assumed that not enough brodifacoum would dissolve in water to create a hazard to aquatic non-target animals. Products used in sewers are water-resistant paraffinized blocks and are not expected to dissolve in water. But hundreds of avian and other wildlife mortalities have been reported across North America [3].

Because of this, it may be interesting to find similar compounds in order to enlarge the spectrum of VKOR inhibitors used today in pest control. We used the Similar Compounds search type of the Chemical Structure Search of the PubChem Compound Database [7] to locate records that are similar to the chemical structure of brodifacoum, using pre-specified similarity thresholds. Using the threshold ≥ than 95% for the similar structures criteria, we found 14 compounds that meet this criteria. In accordance with our calculations and molecular docking simulations, two of these compounds have a better binding affinity to vitamin K epoxide reductase enzyme than brodifacoum, but the binding energy of the other 12 substances is also high, having identical or lower lipophilicity; consequently, they will eliminate faster, possibly lacking a part of the adverse effects.

2. Materials and methods

Hardware: Asus X401A PC, CPU Dual Core Intel 820, 1.7GHz, 4 GB RAM.

Software: OS Windows 7 – 64 bit, Chem 3D Ultra 10.0, ChemDraw Pro 10.0, AutoDock Tools 1.5.6 Molecular Graphics Laboratory The Scripps Research Institute [4], AutoDock Vina by Sargis Dallakyan, The Scripps Research Institute [5], Open Babel 2.3.2. [6], PyRx 0.8, PubChem Compound Database, Firefox 28.0.

The Similar Compounds search type of the Chemical Structure Search of the PubChem Compound Database [7] allows to locate records that are similar to a chemical structure query using pre-specified similarity thresholds. Similarity is measured using the Tanimoto equation and the PubChem dictionary-based binary fingerprint. This fingerprint consists of series of chemical substructure "keys". Each key denotes the presence or absence of a particular substructure in a molecule. The fingerprint does not consider variation in stereochemical or isotopic information. Collectively, these binary keys provide a "fingerprint" of a particular chemical structure valence-bond form.

The degree of similarity is dictated by the Threshold parameter. A threshold of "100%" effectively acts as an "exact match" to the provided chemical structure query (ignoring stereo or isotopic information), while a threshold of "0%" would return all chemical structures in the PubChem Compound database. Various predefined thresholds between 99% and 60% are allowed [7].

Searching the databases (with over 30 million entries) is possible for a broad range of properties including chemical structure, name fragments, chemical formula, molecular weight, XLogP, and hydrogen bond donor and acceptor count. PubChem can be accessed for free through a web user interface.

AutoDock Vina [5] significantly improves the average accuracy of the binding mode predictions compared to AutoDock 4. For its input and output, Vina uses the same PDBQT molecular structure file format used by AutoDock. PDBQT files can be generated (interactively or in batch mode) and viewed using MGLTools. Other files, such as the AutoDock and AutoGrid parameter files (GPF, DPF) and grid map files, are not needed. The docking calculation consists of a number of independent runs, starting from random conformations. Each of these runs consists of a number of sequential steps. Each step involves a random perturbation of the conformation followed by a local optimization (using the Broyden–Fletcher–Goldfarb–Shanno algorithm) and a selection in which the step is either accepted or not. Each local optimization involves many evaluations of the scoring function as well as its derivatives in the position-orientation-torsions co-ordinates. The number of evaluations in a local optimization is guided by convergence and other criteria. The number of steps in a run is determined heuristically, depending on the size and flexibility of the ligand and the flexible side chains. However, the number of runs is set by the exhaustiveness parameter. Since the individual runs are executed in parallel, where appropriate, exhaustiveness also limits the parallelism. Unlike in AutoDock 4, in AutoDock Vina, each run can produce several results: promising intermediate results are remembered. These are merged, refined, clustered, and sorted automatically to produce the final result [8, 9, 10, 11, and 12].

Vina creates *_out.pdbqt files, where it stores all docked poses and scores [5].

The predicted binding affinity of bound structures is given in kcal/mol. To compare the accuracy of the predictions of the experimental structure, AutoDock Vina uses a measure of distance between the experimental and predicted structures, RMSD: root-mean-square deviation.

RMSD values are calculated relative to the best mode and using only movable heavy atoms. For scoring, AutoDock Vina uses a united-atom function, which involves only the heavy atoms [4, 5, and 8].

Two variants of RMSD metrics are provided by the software, rmsd/lb (RMSD lower bound) and rmsd/ub (RMSD upper bound), differing in how the atoms are matched in the distance calculation [5]:

- *rmsd/ub* matches each atom in one conformation with itself in the other conformation, ignoring any symmetry;
- *rmsd'* matches each atom in one conformation with the closest atom of the same element type in the other conformation (rmsd' can not be used directly because it is not symmetric);
- *rmsd/lb* is defined as follows: $\text{rmsd/lb}(c_1, c_2) = \max((\text{rmsd}'(c_1, c_2), \text{rmsd}'(c_2, c_1))$.

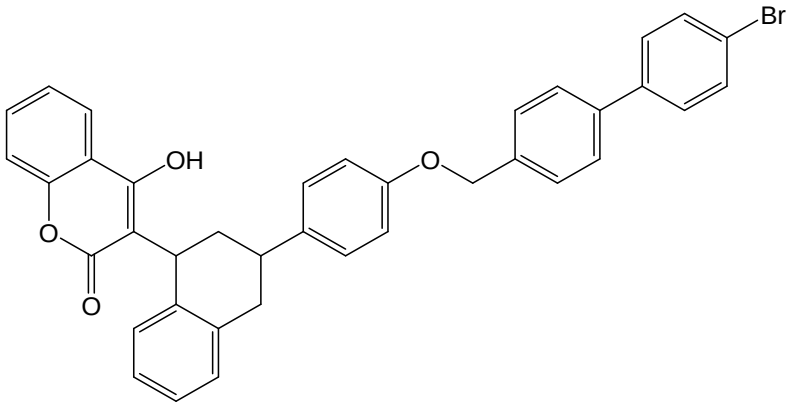
3. Results and discussions

Using the Chemical Structure Search of the PubChem Compound Database [7] and a threshold ≥ than 95% for the similar structures criteria, we detected 14 compounds 95% similar with brodifacoum. We calculated the binding affinities for the ligands (including for brodifacoum) to the surface of the VKOR enzyme. Fourteen substances (with PubChem Compound ID = 54721414, 54721409, 54721416, 54702967, 54702968, 56999900, 54676115, 54716798, 56610083, 56638536, 56629283, 57166454, 57186316, 54736729) are excellent ligands for VKOR. These ligands are shown in *Table 1* and below, together with brodifacoum (CID 54680676).

Table 1. The 14 ligands with a similarity threshold ≥ 95%, and brodifacoum (54680676)

PubChem CID [7]	**IUPAC Name**	**Molecular Formula**	**MW [g/mol]**	**XlogP3**
54721414	3-[3-[4-[[4-(4-bromophenyl)phenyl]methoxy] phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{38}H_{29}BrO_4$	629.53846	9.1

PubChem CID [7]	**IUPAC Name**	**Molecular Formula**	**MW [g/mol]**	**XlogP3**
54721409	3-[3-[4-[4-[(4-bromophenyl)methoxy]phenyl] phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{38}H_{29}BrO_4$	629.53846	9.1
54680676	3-[3-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
54721416	3-[3-[4-[[4-(4-bromophenyl) phenyl]methyl] phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{38}H_{29}BrO_3$	613.53906	9.6
54702967	3-[3-[4-[2-(4-bromophenyl)ethyl]phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{33}H_{27}BrO_3$	551.46968	8.2
54702968	3-[3-[4-[(4-bromophenyl)methoxy]phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{32}H_{25}BrO_4$	553.4425	7.5
56999900	3-[[4-(4-bromophenyl)phenyl]-cyclohexylmethyl]-4-hydroxychromen-2-one	$C_{28}H_{25}BrO_3$	489.4003	7.6
54676115	3-[(1S,3R)-3-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
54716798	3-[(1R,3R)-3-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-1-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
56610083	3-[(2S,4R)-4-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-2-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
56638536	3-[(2R)-4-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-2-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
56629283	3-[(2S)-4-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-2-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
57166454	3-[1-[4-(4-bromophenyl)phenyl]-2-phenylethyl]-4-hydroxychromen-2-one	$C_{29}H_{21}BrO_3$	497.37924	6.8
57186316	3-[(2S)-1-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-2-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6
54736729	3-[(2R,4R)-4-[4-(4-bromophenyl)phenyl]-1,2,3,4-tetrahydronaphthalen-2-yl]-4-hydroxychromen-2-one	$C_{31}H_{23}BrO_3$	523.41652	7.6



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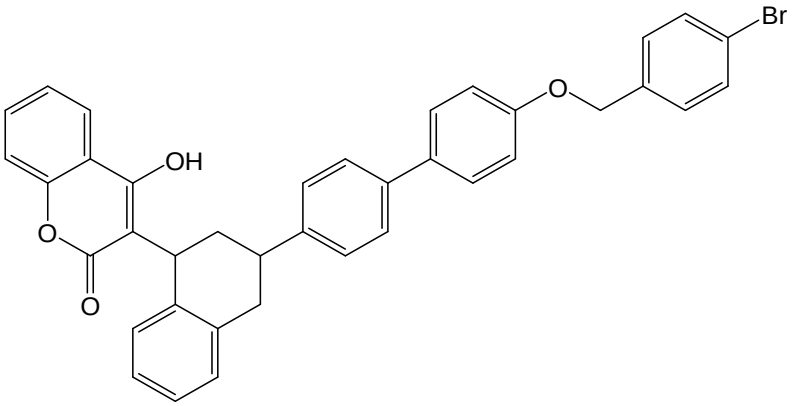

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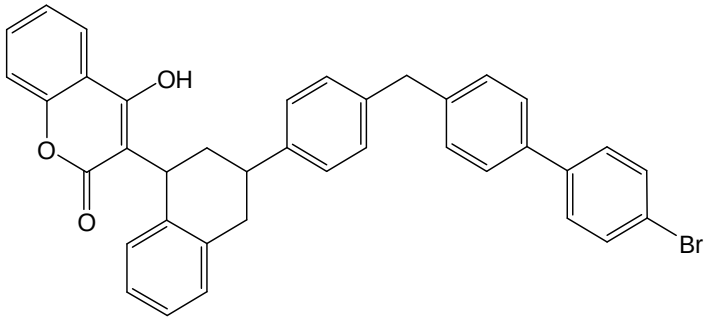

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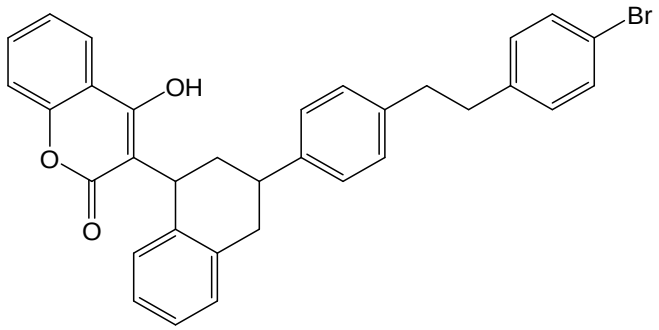

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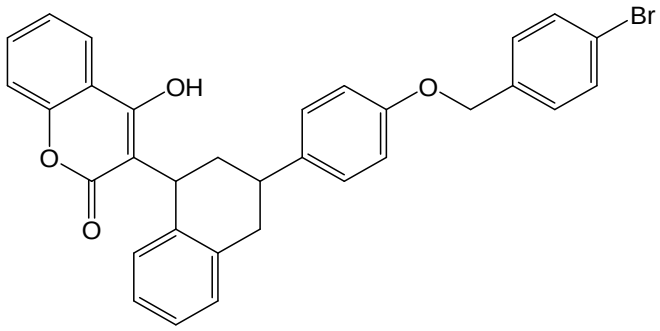

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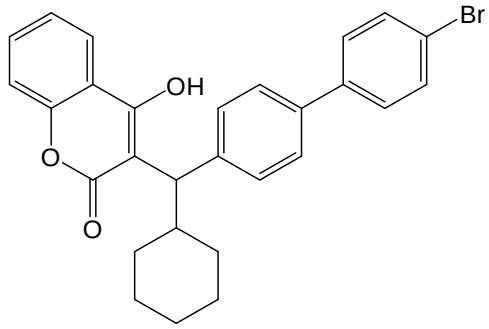

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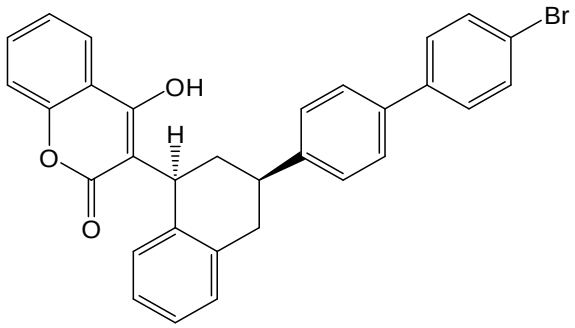

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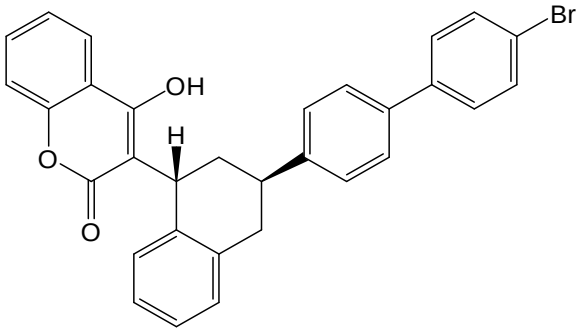

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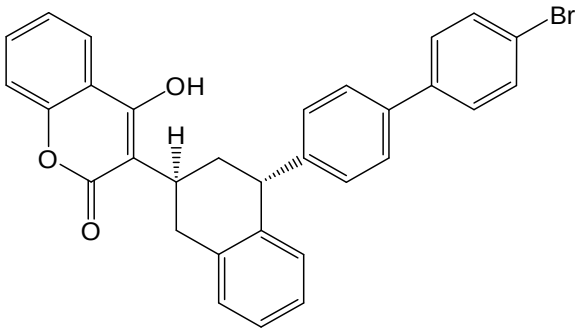

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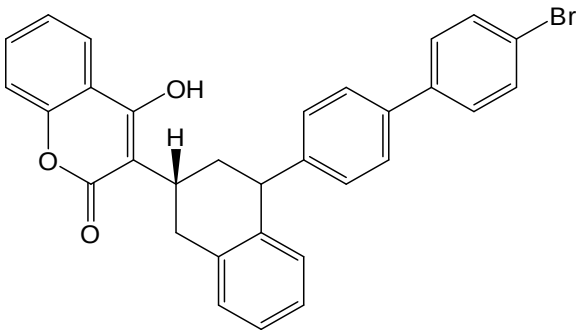

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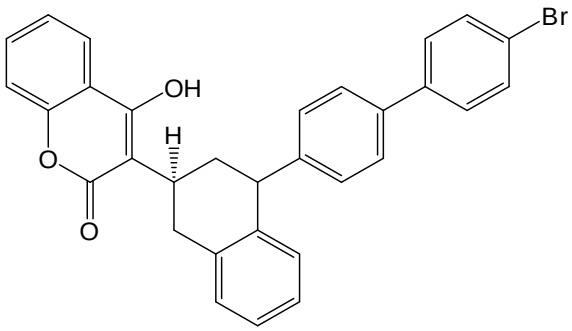

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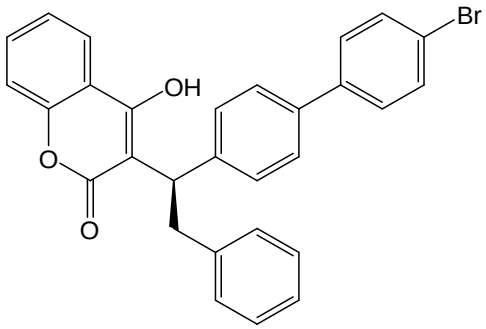

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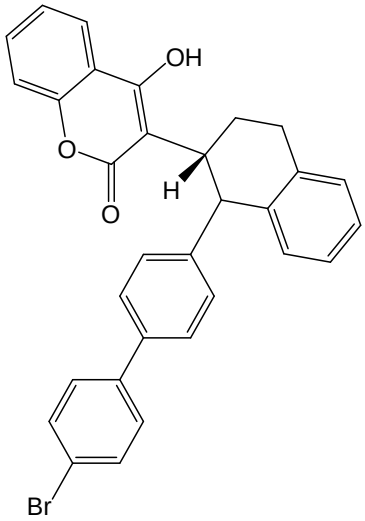

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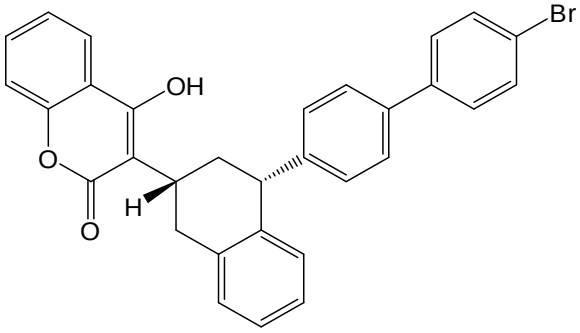

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In *Table 2*, there are presented the calculated binding affinities in descending order for the ligands and the enzyme VKOR (PDB code 3KP9 [13]).

When using a flexible docking engine, then minimizing the input conformation of the ligands can reduce problems that are known to occur in conformer generation inside the docking engine, which arise if the input 3D conformation is not relaxed into good bond lengths and angles. For small molecules, a good choice is to use some of the molecular mechanics to optimize the structure down to a local energy minima like UFF or mm2. The assignment of

Universal Force Field (UFF) atom types and the calculation of the molecular connectivity (identifying bonds, angular, torsional and inversion terms) has been performed using the routines available in the Open Babel package [5, 6]. Open Babel can be used for refining initial geometries with UFF molecular-mechanics optimizations, adding or removing hydrogens to PDB protein files, and many other utility tasks that often arise in molecular modelling projects.

Open Babel supports a number of force fields which can be used for energy evaluation as well as energy minimization. We used the following energy minimization parameters: Conjugate Gradients optimization algorithm, 200 total number of steps; stop if energy difference is less than 0.1 kcal/mol.

The virtual screening results show that the 14 compounds (*Table 2*) are strong inhibitors of VKOR. The structure of enzyme was retrieved with Chem 3D's Online Find Structure from the PDB ID option. The water molecules, other small molecules, such as solvent molecules and other relics of the isolation and crystallization procedures, were removed.

X-ray crystallography usually does not locate hydrogens, hence most PDB files do not include them. But hydrogens, particularly those that can form hydrogen bonds, are important in binding ligands; so, hydrogens were added to backbone N and to amine and hydroxyl side chains. Atoms were renumbered, and PDBQT files were generated with AutoDock Tools 1.5.6.

Table 2. The calculated binding affinities (including brodifacoum, CID = 54680676) in descending order for the enzyme VKOR (3KP9).

Enzyme-Ligand	**Binding affinity** [kcal/mol]	**rmsd/ub** [Å]	**rmsd/lb** [Å]
3KP9_54721414_mmff94_E=259.03	-11.3	0	0
3KP9_54721409_mmff94_E=203.54	-10.6	0	0
3KP9_54680676_mmff94_E=162.68	-10	0	0
3KP9_54721416_mmff94_E=182.96	-9.8	0	0
3KP9_54702967_mmff94_E=172.60	-9.5	0	0
3KP9_54702968_mmff94_E=173.00	-9.5	0	0
3KP9_54721416_mmff94_E=182.96	-9.5	2.003	1.139
3KP9_54716798_mmff94_E=880.70	-9.3	0	0
3KP9_56999900_mmff94_E=1010.91	-9.3	0	0
3KP9_54676115_mmff94_E=880.70	-9.2	0	0
3KP9_56610083_mmff94_E=954.18	-9	0	0
3KP9_56638536_mmff94_E=956.00	-9	0	0
3KP9_56629283_mmff94_E=881.16	-8.7	0	0
3KP9_57166454_mmff94_E=125.89	-8.7	0	0
3KP9_57186316_mmff94_E=884.05	-8.7	0	0
3KP9_54736729_mmff94_E=903.33	-8.1	0	0

The RMSD cut-off of 2Å is usually used as a criterion of the correct bound structure prediction [14]. Using the same cut-off value, the two metrics used for RMSD (summarized in *Table 2*) indicate that 2 compounds are better ligands of VKOR than brodifacoum (CID 54680676) because they require lesser energy for binding. This suggests that these substances will successfully substitute brodifacoum. The binding energy of the other 12 substances is also high, having identical or lower lipophilicity; consequently, they will eliminate faster, possibly lacking a part of the adverse effects.

We used the default docking parameters:

– number of binding modes: 9,
– exhaustiveness (thoroughness of search): 8.

Larger values increase the probability of finding the global minimum, but they also extend the computational time. Increasing the exhaustiveness value increases the time linearly and decreases the probability of not finding the minimum exponentially. Apart from exhaustiveness influenced by users, Vina has an internal heuristic algorithm to extend the search in accordance with an increasing number of atoms and rotatable bonds [15].

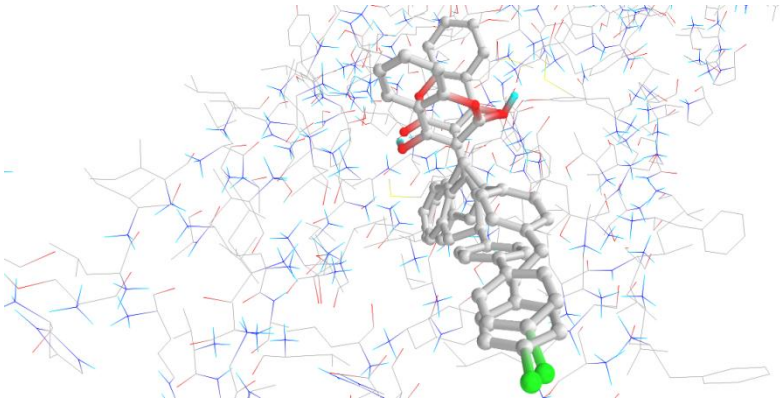

Figure 1. Molecular docking of brodifacoum (CID 54680676) and the ligand CID 54702968 in protein target (Mayavi).

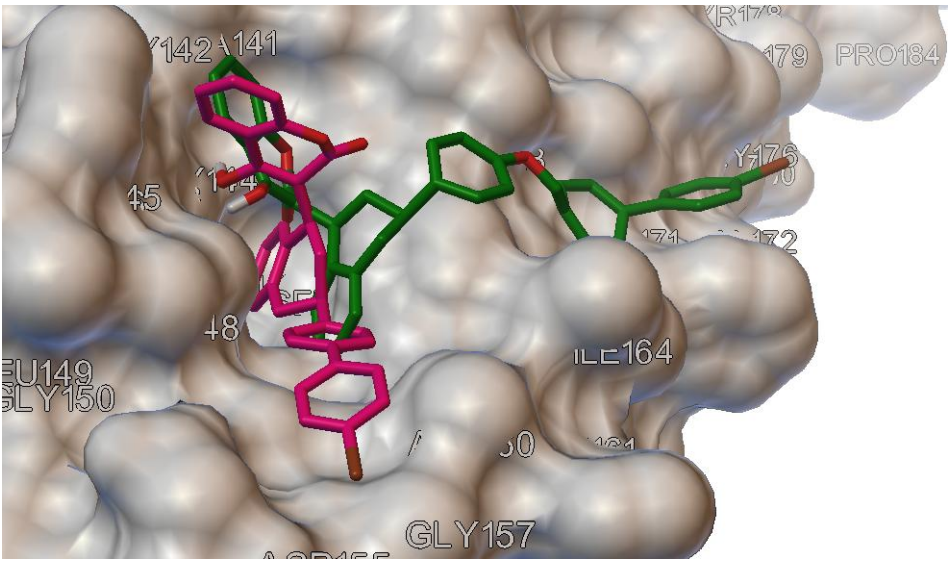

Figure 2. Ligand CID 54721414 and brodifacoum (CID 54680676) on the binding site of VKOR (Autodock).

Conclusion

Compounds with PubChem ID: 54721414, 54721409, 54721416, 54702967, 54702968, 56999900, 54676115, 54716798, 56610083, 56638536, 56629283, 57166454, 57186316, and 54736729 have good binding affinity to vitamin K epoxide reductase enzyme and they present the correct bound structure prediction; so, they seem to act alike and to be good substitutes for brodifacoum. Further investigations are needed to establish their pharmacodynamic properties and toxicity.

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A historical survey of the Corunca Castle, Romania, based on the military survey maps and present-day measurements

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Abstract. Corunca is situated at 4.5 km SE from Târgu-Mureș, near the Salt Stream, the Bozeni Stream, and the Vațman Stream. Its area is inhabited from ancient times. Both prehistoric and Roman findings were reported to have been found within the village boundaries. Its neighbouring medieval village, Sárvári, perished in the 16th century, while Kisernye was devastated by Turkish troops in 1661. The settlement was first recorded in 1332 as *Korunka*. The Reformed Church was built between 1769 and 1778, while its spire dates from 1793. The earlier church was surrended by high protective walls, which were demolished in 1769.

The extremely ruinous castle with its neoclassical façade and a couple of neighbouring farm buildings appear on the left side of the European route E60 travelling from Târgu-Mureș to Sighișoara. Today, this is a barren place, although once it was surrounded by a grove the size of 120 cadastral acres [2].

During the reign of John Sigismund Zápolya, Prince of Transylvania and ruler of a part of the Kingdom of Hungary, the village belonged to Thomas Mihályfy. The castle was ravaged in 1562 by the revolted Szeklers. After the fall of the Mihályfy family, the Chancellor of Transylvania, Farkas Kovacsóczi owned the estate, which later came down to the Tholdalagi family. The Tholdalagi family belongs to one of the great magnate families of Transylvania, with nicknames deriving from Ercea and Iclod, but originating from Toldal, Mureș County, Romania – their ancient demesne from the 16th century. Mihály I. Tholdalagi (1580–1673), one of the wisest diplomats in the Principality, reshaped the original building to an impressive castle in the 1630s, whose size and adjoining buildings are described in the Inventory dating from 1680. The first members of the Tholdalagi family came to Transylvania from Hungary. According to the family traditions, and also mentioned in their Certificate of Count, their ancestor is the extinguished Alaghi family member, András, who obtained Toldalag settlement together with its neighbouring Ercse in

1453; hence the nickname “Ercsei”. Thus, Mihály Tholdalagi’s parents were Balázs from Gáldtő and Borbála Bessenyei [1].

Keywords: Castle, Corunca, revitalization, garden, hystory

1. The history of the castle and its garden

The ancient castle was ravaged by the Szeklers during the reign of John Sigismund Zápolya, Prince of Transylvania, in 1562. More than a century later, Mihály Tholdalagi, the new owner of the estate, had it completely rebuilt. Ferenc Tholdalagi, one of the descendants of the Count, extended it in 1829, based on the plans of Joseph Weixlbraun. The building, having a U-shaped ground plan, was completed with a 50-metre neoclassical façade, with semi-cylindrical, coffering, barrel vault style passage in its median avant-corps of the central axis. The proportional dimensions and subdued decorations place the castle among the most beautiful classicist-style castles (Fig. 1.) [3].

Figure 1. The Corunca Castle from 1930

The demesne in Corunca was much more beautiful and modern than the one in Mănăstirea, Cluj County, Romania. The castle and its outbuildings stand out in the first military survey map (1769–1773), and the park was already taking shape (Fig. 2). A full picture is offered about the castle and its beautiful English park by the second (1806–1869) and third (1869–1874) military survey maps.

Figure 2. The military map of Corunca (Josephinische Aufnahme 1769–1773)

The dwelling-house was designed by an uncle, Colonel Roke-pine Baron, resulting in a very simple outlook, but a highly comfortable interior. Tall rooms with high ceilings, modernly furnished, with parquet, painted walls, even wallpaper in two of the rooms, and the furniture coming from the Vienna of the 1830s. Men-servants in livery adorned with braids formed in the family crests, except for my father's hussar bodyguard dressed in full regalia resembling a general of the cavalry. The English garden was the most beautiful place, larger in size than the one in Schönbrunn, with artistically planted gorgeous bushes and trees. The heydays of Corunca were in the years of 1846–1848. My father's fortune was really huge then… Although the household was smaller than at my grandfather's, it was more refined and elegant. First and second cook, three kitchen boys, a royal servant from my mother, my father's hussar bodyguard, three lackeys, a Viennese chief gardener, four gardeners, a Hungarian vegetable gardener, and Gipsies when needed for pottering in the garden. It was a splendid park! I can see it even now, and feel the warm, stuffy evenings laden with the scent of magnolia and dates. Nowhere else have I seen so many magnolia trees or heard so many nightingales sing as in that garden. My father used to go to Vienna almost each year; though it took as much as 8 to 10 days to get there, he would still set off. These trips refined his taste; he kept bringing something new for the house and the garden... And he did a great job. Due to his office, he had to stay a lot at home managing his demesne in an exemplary way, my good old mother being so happy. Hardly ever

did we have disquiet later, when my father spent time in Vienna more than with us, thus abandoning his wife, family and the estate, which fell into decadence. As a husband and father, he always behaved gallantly [4].

The rooms were decorated with contemporary furniture, mirrors, chandeliers, and carpets. The last of the white porcelain stoves was saved by Gyula Keresztes, a retired architect from Târgu-Mureş, who brought it to the county seat's Registry of Marriages. The library of the Tholdalagi Castle was considered to be one of the largest libraries in Transylvania, visited with pleasure by noblemen from Târgu-Mureş. The shelves were filled with incunabula and book rarities. A part of the collection is stored in the Teleki–Bolyai Library in Târgu-Mureş. Art historian József Bíró writes in his book Transylvanian Castles (Erdélyi kastélyok) that the quondam crypt of the Tholdalagi family built in the hill-side was destroyed during a landslide, and it was rebuilt in 1806. The Hungarian and Latin inscriptions of the tombstones, marble tables, and sarcophagus were copied and published in full by historian Mihály Spiellmann. Found accidentally, the family crypt completes the records of the family generations and last but not least it increases the monument value of the Corunca Castle. The last resident of the castle was Count József Tholdalagi, who left the premises in 1944, which was later used as a grain storage facility.

The present state of the castle and its garden

The Corunca Castle will soon enrich the list of perished architectural heritage unless restoration starts – concludes Gyula Keresztes, speaking of the castle rebuilt almost two hundred years ago.

Once the castle was surrounded by a grove of deciduous trees on 120 cadastral acres with a fish pond. Today, these are replaced by mounds, rich soup of mud, and a depressing industrial plant built in the Communist era. The memory of Count Mihály Tholdalagi is only preserved in the history, the local school bearing his name, and by the ruins. New inhabitants with their castles spinning around on a golden duck's leg in this "urbanizing" settlement may not even know that the land once belonged to one of the most talented diplomats at the end of the 17th-century Transylvania. The expert, together with his colleague Dezső Csákány, did anything posssible in the last three or four years so that the residence of Count Tholdalagi should have a different fate than the ones in Sânpaul, Boiu, or Cristești. As he said, countless promises had been made by the new French owner of the building and his representative, who mostly stayed in Romania. What is more, Alain Vigneau, who runs the ProMobDecor joiner-shop in the outbuildings, requested expert opinions twice on behalf of Chair Claude Moscovici, and then asked for a price quote for design. However, as time went by, both the art historian and the local mayor came

to the conclusion that the French owner was either frivolous or did not have financial resources.
The park completely disappeared around the castle, and the land was ploughed. The landmark is inexistent, evidenced by the attached geodetic survey (Fig. 3).

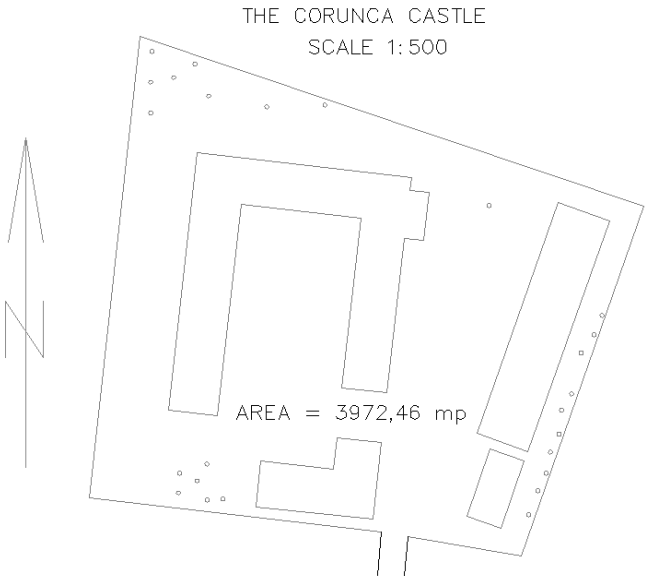

Figure 3. The actual plan of the castle and its garden

According to Géza Keresztes, both the owner and the local government are to be blamed for the present state. A member of the National Committee for Historical Monuments, Sibiu Regional Committee, stated that under the acting laws the owner could have been forced by the mayor's office to conserve the building, and upon infringement a fine could have been imposed. According to the Historical Monuments Act, if nothing happens after several warnings, the municipality can recommend its nationalization. Although the site is in poor condition, having lost its horticultural importance, the historical significance of the place is beyond any doubt. No one would say that medieval castle ruins are not to be protected just because they are in ruins. However, the true value of the Corunca Castle lies in the well-established position of the Tholdalagi family's historical significance. Therefore, it should be considered a monument and it is a public interest to save it.

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Erratum

In the published articles Acta Universitatis Sapientiae Agriculture and Environment (2014) 6. (pages 24–32) *M. Gulyás, M. Fuchs, I. Kocsis, Gy. Füleky*: *Effect of the soil treated with biochar on the rye-grass in laboratory experiment* and (pages 33–38) *G. Rétháti, A. Vejzer, B. Simon, R. Benjared, Gy. Füleky*: *Examination of zinc adsorption capacity of soils treated with different pyrolysis products,* we used an incorrect form of the origin of the samples.

In this erratum, we provide a revised Acknowledgement and References in the text.

The results and the biochar sample originate from the EU FP7 REFERTIL 289785 project [*www.refertil.info*] *and Terra Humana Ltd.* [*www.3ragrocarbon.com*], *and at relevant sections: "The REFERTIL* (*289785*) *Collaborative project is co-funded by the European Commission, Directorate General for Research, within the 7th Framework Programme of RTD, Theme 2 – Food, Agriculture and Fisheries, and Biotechnology."*

We aplogize for any inconvenience caused.

(The editors)

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