Research Article

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Analysis of Spontaneous Symmetry Breaking phenomenon in QFT

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Abstract

Symmetry plays a very vital role in physical system and it helps in understanding various phenomenon of nature. Beauty of symmetry lies not only in its original form but when it is broken (due to some external reasons) then also it opens doors to understand other related phenomenon. So, study of symmetry is like study of physics only. Concept of symmetry and its breaking helps in understanding very important phenomenon in physics like Superconductivity, phase transition in Ferromagnetism and mass generations of Bosons due to Higgs mechanism etc. The underlying mathematical model for symmetry analysis and its breaking is same in every phenomenon.

This report provides a detail explicit mathematical calculation of the different vacuum states (minima) of a Quantum Field Theoretical (QFT) model of 4D Lagrangian density, $\mathscr{L}$ of a complex scalar field (with a quartic interaction). These results are supported by the computational work which simulate the resulting potential depicting all points of minima. It is reported that the above system has degenerate vaccua as the locus of a ring in the complex plane for the mass parameter, m2< 0.This leads to the onset of Spontaneous Symmetry Breaking (SSB) in the potential term due to the breaking of gauge symmetry of the potential. This is a very interesting phenomenon because SSB plays an important role in Higgs Mechanism which is supposed to generate or attributes mass to all the particles (with mass) existing in the universe.

Keywords: Symmetry, QFT, Lagrangian density, quartic scalar fields, vacuum states, SSB

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1. Introduction

Physics associated with the study of symmetry is very rich, profound and interesting. It requires an elaborate discussion and presentation with the larger spectrum of audiences ranging from post graduate students to high end researchers. In physics, practically all great conservation laws of nature are due to existence of some sort of symmetry or invariance. As per Noether's theorem for every continuous symmetry there is a corresponding conserved current (energy, momentum, angular momentum etc.). Nobel laureate P. A Anderson in his famous article More is Different published in Science (1972) [1] quoted that "It is only slightly overstating the case to say that physics is the study of symmetry". This shows that why symmetry is so important aspect of nature and it demands a

details study both theoretical as well as experimental. Nature loves symmetry and it is inherent in its body and soul. Governing laws of nature and theories not only valid for its existing symmetries but to the breaking of its symmetries also. This negative aspect (breaking)of symmetry is equally important in explaining various phenomenon of our universe. There are various mechanisms in nature wherein the symmetry can be hidden or broken. A more profound way of hiding symmetry is the phenomenon of spontaneous symmetry breaking. In this, laws of physics are symmetric but the ground (vacuum)state of the system does not respect the overall symmetry of the system.

Some examples of SSB from everyday life is suppose there is a spinning coin on a table and it can land either on its head or tail and it has no preferred choice for such landing. Both landing is equally probable (50-50 chances). As long the coin is rotating it has the symmetry or freedom of choice to land on any one side. Once it stopped spinning and choose to land on head or tail (minima or vacuum state) the initial symmetry is broken and system undergoes a SSB and initial symmetry of the system is no longer available to it.

Another, similar example is people sitting on a round dining table and they are symmetric (rotational) w.r.t the centre of the table. If any one person uses his left or right hand to pick up a spoon or plate then spontaneously the rotational symmetry is broken and system undergoes SSB as it chooses one particular state.

Phenomenon of SSB occurs in various fields like Material Science, High energy (particle) physics etc [2].Initially this concept was introduced by Landau to explain magnetic phase transition in Ferromagnets. In Ferromagnets all the atomic dipole moments are arranged either up or down and resulting in development of net magnetisation, M. When the temperature rises above the critical temperature $(T > T_c)$, Ferromagnets lose their net magnetisation and dipoles are randomly oriented owing to thermal energy and system becomes random and chaotic due to decrease in symmetry. The system acquired a radial symmetry (all directions are equally probable). The minima for this configuration occur at $M = 0$ only (single value).

When system is cooled down $(T < T_c)$, dipole moments start arranging themselves in up or down positions (both positions are equally probable) and a net magnetisation M is regained and system becomes ordered as initial symmetry is regained. M is acting as the order parameter for the given system. In the vicinity of T_c both the events occur. For $T < T_c$, system has minima at two different values of $M = +t, -t$ (t is symmetry breaking parameter for this system). $M = 0$ minimum state is no longer available in this case. Thus below T_c system falls spontaneously in one of the two minima values of the order parameter $M(\neq 0)$ available to them and thus breaking the radial symmetry of the original configuration. This loss or breaking of the symmetry leads to gain in the overall order of the system as value of the ordered parameter M increases.

Landau's path breaking concept of SSB is introduced to particle physics (Standard Model/ Electroweak theory) by Peter Higgs in 1960. He gives the concept of Higgs potential (H), Higgs Boson and postulated Higgs mechanism, which through SSB imparts

masses to Higgs Bosons (W & Z). It is proposed that universe undergoes a SSB as it was cooling due to loss of energy during expansion. Just after the 10^{-11} s of the Big Bang explosion the universe undergoes SSB and slowly all the particles like electron, proton, neutron etc (initially they were massless) starts gaining their masses and formation of atoms takes place. Also, all the fundamental forces of nature (gravity, electromagnetism, strong and weak) got separate out from each other and loses their unified identity/ nature which they believed to have just before the onset of Big Bang. So SSB plays an important role in the formation and space time fabric of the universe in the present form as we see it today.

Since inception of the universe our mother nature playing and hiding with its symmetries and showing its different colours through its mistry particles (like God particles which is supposed to give masses to all the particles in the universe) and still it is holding many unsolved mysteries in its womb waiting to be revealed by the mankind in due course of time. Many new hidden symmetries may be discovered as the Grand Unification Theory (GUT) is still not taken its final shape and formulations. SSB theories may open many doors like here also. In order to verify the GUT theories, we have to create the situation in the lab with such a humongous amount of energy or temperature (10^{15} GeV) at which SSB was just set in (at least).

So, I choose this exciting phenomenon to work on it and write this article. This article will aid in the understanding the concept of SSB and its mathematical models (simulation etc.) in QFT (vacuum states and its derivations) and how the phenomenon of SSB occurs resulting in fascinating phenomenon like Higgs mechanism etc. This is particularly important for the university teachers &students of M.Sc. courses and beyond to understand above phenomenon in detail and lucid manner. Most of the available text books on Quantum Field Theory (QFT) [3] mention only about the ground states of a 4D complex scalar field (spin=0) with the quartic self-interaction terms for various values of its mass parameter (m). They do not show the explicit mathematical calculations through which different values of the ground states (minima) of such scalar fields are obtained. For a beginner, who just delved into the QFT field becomes quite difficult to understand or conceptualise the mathematical origin of these statements made in these standard reference books on QFT [4]. In this report a detailed mathematical calculation and simulations were done to give more insight in to the calculation of the ground states of a scalar complex field about its origin and physical interpretation through different types of plots (2D, 3D, ellipsoid of revolution etc). Such detailed mathematical approach to this problem is not reported yet.

2. Mathematical Preliminaries and methodology

In the free field theory, simplest form of Lagrangian density, $\mathcal{L}_0$ for a complex scalar field ($\emptyset$) and $\emptyset^*$ is complex conjugate of $\emptyset$ with m as the mass (parameter) of the field, is given by

$$\mathcal{L}_0 = (\partial_\mu \emptyset)(\partial^\mu \emptyset^*) - m^2(\emptyset^* \emptyset) \dots \dots \dots \dots (1)$$

If we use this simple form of Lagrangian then we will obtain an equation of motion for scalar field $\emptyset$. This classical field also satisfies, Klein-Gordon (KG) equation. In this field, particles (zero spin) can only be excited or de-excited to given available energy states (satisfying certain

underlying conditions) but they do not interact among themselves. Thus, such free field can only give emission or absorption spectra. Here number of particles involved remains conserved I,e creation or annihilation of particles is not allowed.

If we add or include higher order terms like $\mathcal{L}_{int.}$ in this free field Lagrangian and it can be treated as a weak perturbation to the given system (assuming valid at all energy regime). Then such perturbed Lagrangian results in the crop of very interesting phenomenon called interaction among the field particles themselves and it is known as self-interaction.

Thus, new Lagrange is now, $\mathcal{L}_{new} = \mathcal{L}_0 + \mathcal{L}_{int.}$, Where $\mathcal{L}_{int.}$ is the interaction Lagrangian density term (perturbation).

If we are working in a low energy interaction regime, then we can consider $\mathcal{L}_{int.}$ as quartic interaction which is type of self-interaction in a scalar field. Quartic interaction term is represented by $\mathcal{L}_{int.} = -\lambda(\emptyset^*\emptyset)^2$, derived from weakly coupled $\emptyset^4$ theory [**5**]. This term induces interaction among the field particles and gives rise to many interesting phenomena like particle creation or annihilation, which means that total number of particles does not remain conserved unlike in earlier case. λ (>0) is known as the coupling constant for the given interaction.

Thus, we can write new Lagrangian density, eqn. (1) as below

$$\mathcal{L}_{new} = \mathcal{L} = (\partial_\mu\emptyset)(\partial^\mu\emptyset^*) - m^2(\emptyset^*\emptyset) - \lambda(\emptyset^*\emptyset)^2 = (\partial_\mu\emptyset)(\partial^\mu\emptyset^*) - V(\emptyset,\emptyset^*) \qquad (2)$$

This can be treated as an effective quantum field theory (EQFT) in low energy interactions.

Total potential is now, $V(\emptyset,\emptyset^*)=m^2(\emptyset^*\emptyset) + \lambda(\emptyset^*\emptyset)^2 = m^2|\emptyset|^2 + \lambda|\emptyset|^4$

Here mass term is very important, later, we will see that when $m^2 < 0$, the last quartic (interaction) term is responsible for spontaneous symmetry breaking of the potential $V(\emptyset,\emptyset^*)$ so it is also known as the symmetric breaking parameter. This parameter decides whether the given potential term will undergo spontaneous breaking or not.

Now, the complex field $\emptyset$ can be expressed as a combination of real and imaginary parts as follows,

$$\emptyset = \frac{1}{\sqrt{2}}(\emptyset_1 + i\emptyset_2, \emptyset^* = \frac{1}{\sqrt{2}}(\emptyset_1 - i\emptyset_2) \qquad (3)$$

If we put eqn. (3) in eqn. (2), we obtain after simplification that

$$\mathcal{L} = \frac{1}{2}(\partial_\mu\emptyset_1)(\partial^\mu\emptyset_1) + \frac{1}{2}(\partial_\mu\emptyset_2)(\partial^\mu\emptyset_2) - \frac{m^2}{2}(\emptyset_1^2 + \emptyset_2^2) - \frac{\lambda}{4}(\emptyset_1^2 + \emptyset_2^2)^2 \qquad (4)$$

The potential function $V(\emptyset,\emptyset^*)$, from the above is now reduced to

$$V(\emptyset_1,\emptyset_2) = \frac{m^2}{2}(\emptyset_1^2 + \emptyset_2^2) + \frac{\lambda}{4}(\emptyset_1^2 + \emptyset_2^2)^2 \qquad (5)$$

The above potential now depends upon the values of two scalar fields $\emptyset_1 and\ \emptyset_2$.

Now our aim is to find the vacuum state or ground state energy of the given potential $V(\emptyset,\emptyset^*)$. This requires to find the extrema of the above potential. As per calculus, for maxima, the second derivative should be negative at the point where first derivative is zero. First derivatives are calculated as below

$$\frac{\partial V}{\partial\emptyset_1} = m^2\emptyset_1 + \lambda\emptyset_1(\emptyset_1^2 + \emptyset_2^2), \qquad \frac{\partial V}{\partial\emptyset_2} = m^2\emptyset_2 + \lambda\emptyset_2(\emptyset_1^2 + \emptyset_2^2)$$

Their corresponding second derivatives will be calculated as

$$\frac{\partial^2 V}{\partial \phi_1{}^2} = m^2 + \lambda(3\phi_1^2 + \phi_2^2) = r(\text{say}) \qquad (6)$$

$$\frac{\partial^2 V}{\partial \phi_2{}^2} = m^2 + \lambda(3\phi_2^2 + \phi_1^2) = t \qquad (7)$$

$$\frac{\partial^2 V}{\partial \phi_1 \partial \phi_2} = 2\lambda \phi_1 \phi_2 = s \qquad (8)$$

For two variables $\phi_1 and\, \phi_2$, we have to determine the sign of the quantity

$(rt - s^2)$. This will decide the corresponding extremum values.

$$\text{setting } \frac{\partial V}{\partial \phi_1} = 0 \text{ and } \frac{\partial V}{\partial \phi_2} = 0$$

This will in turn gives,

$$\phi_1[m^2 + \lambda(\phi_1^2 + \phi_2^2)] = 0 \qquad (9)$$

$$\phi_2[m^2 + \lambda(\phi_1^2 + \phi_2^2)] = 0 \qquad (10)$$

From eqn (9) and (10) we can conclude possible solutions are

$\phi_1 \& \phi_2 = 0$ (local minima) & $[m^2 + \lambda(\phi_1^2 + \phi_2^2)] = 0$ if we assume $\phi_1^2 + \phi_2^2 = \mu^2\ (say)$

then$[m^2 + \lambda\mu^2] = 0$ or$\mu^2 = {}^{-m^2}/_{\lambda}$

Now,$m^2 < 0$ or$m^2 > 0$ so two different cases arises and all these possible cases are further explained under different sub categories as below.

Case 1: $m^2 > 0$,

In this case bracketed terms in eqn. (9), (10) will always be positive non zero term I,e

$m^2 + \lambda(\phi_1^2 + \phi_2^2) \neq 0$.

Then solution from eqn. (9), (10) will be given by

$\Rightarrow \phi_1 = 0 \,\&\, \phi_2 = 0$

Thus, in the complex plane, $O(0,0)$ is an extremum point. At this extremum point we have to calculate the value of the quantity $(rt - s^2)$ as follows

$(rt - s^2) = [m^2 + \lambda(3\phi_1^2 + \phi_2^2)]\ [m^2 + \lambda(3\phi_2^2 + \phi_1^2)] - 4\lambda^2\phi_1^2\phi_2^2$

$= m^4 + other\ terms > 0. \qquad (11)$

Thus, the value of $(rt - s^2)$ is positive so the sign of r will decide whether the point $O(\phi_1, \phi_2)$ is maxima or minima.

If $r > 0$, (ϕ_1, ϕ_2) is minima

$r < 0$, (ϕ_1, ϕ_2) is maxima

It can be explicitly checked that

$$r = m^2 + \lambda(3\phi_1^2 + \phi_2^2) = m^2 + (other\ terms) > 0.$$

Thus, the point $O(0,0)$ in complex plane of $\phi_1 and\, \phi_2$ is point of minima as shown in fig. (1).

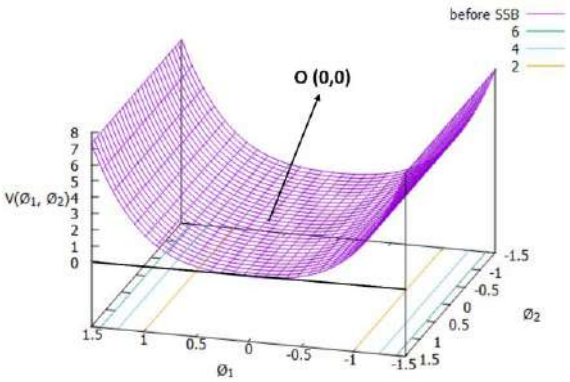

Fig. 1. 2D plot of the potential $V(\phi_1, \phi_2)$ with origin at $O(0,0)$ for $m^2 > 0$

Potential $V(\phi_1, \phi_2)$ at point $O(0,0)$ is symmetric so the corresponding ground state

lying at the origin is also symmetric under global ($\theta = constant$) continuous $\cup(1)$ gauge transformations as below

$$\emptyset(x) \rightarrow \emptyset'(x) = \emptyset(x)e^{-i\theta} \qquad (12)$$

$$\emptyset^*(x) \rightarrow (\emptyset^*)'(x) = \emptyset^*(x)e^{i\theta} \qquad (13)$$

Which happens to be a continuous symmetry of the starting Lagrangian density of eqn. (2). As a consequence, ground state is also found to satisfy the above continuous $\cup(1)$ gauge symmetry. Thus, we conclude that there is no SSB for the case $m^2 > 0$.

Case 2: $m^2 < 0$,

This is the most important case among all and it leads to many interesting & complicated phenomena. Case 2 has been further sub divide into sub cases (2.1 &2.2), depending on the possible set (two) of solutions to the eqns. (9) & (10).

Case 2.1: $\emptyset_1 = 0$, $\emptyset_2 = 0$. This corresponds to the point $O(0,0)$, origin of the complex plane. At this point following conditions are satisfied, namely

$$rt - s^2 = m^4 > 0 \qquad (14)$$

& $r = m^2 < 0$

This shows that, unlike the previous case, here $r < 0$ (negative). Thus, the point $O(0,0)$ now here corresponds to the point of maxima instead of minima as we have in case 1. Thus, the origin is lifted up (excited) from the known groundstate and it no longer corresponds to the ground state (vacuum) thus breaks the ground state symmetry it enjoyed in the previous case. This result is graphically shown in fig. (2)

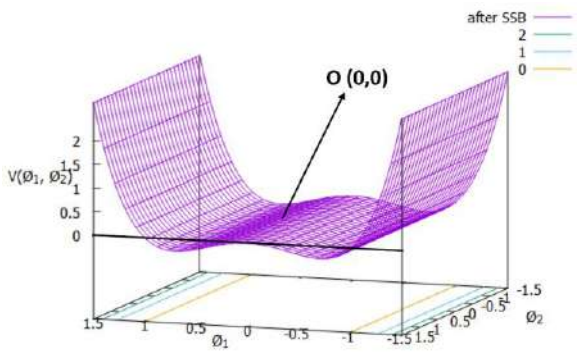

Fig. 2. 2D plot of $V(\emptyset_1,\emptyset_2)$ for $m^2 < 0$.

Case 2.2. $\emptyset_1 = \widetilde{\emptyset_1}, \emptyset_2 = \widetilde{\emptyset_2}$(set of probable solution)

This reduces the original eqns. (9), (10) to the following eqns. (15), (16) respectively as.

$$[m^2 + \lambda(\emptyset_1^2 + \emptyset_2^2)] = 0 \qquad (15)$$

$$[m^2 + \lambda(\emptyset_1^2 + \emptyset_2^2)] = 0 \qquad (16)$$

When we solve the eqn. (15) & (16) we will get infinite number of solutions for the pair $\emptyset_1 and\ \emptyset_2$. Now we will have to dig out the possible ground states from this infinite number of probable solutions. We have to use Taylor Series to find the extrema values as we have done from basic mathematics (partial derivatives with two variables) [**6**]. Any function, $f(x,y)$ will have maxima or minima at point $x = a, y = b$ according to condition,

$f(a+h, b+k) < f(a,b)$for maxima
$> f(a,b)$for minima (17)

Alternately, if $\Delta f = [f(a+h, b+k) - f(p,q)]$ is of the same sign for all small values of h,k and if the sign is negative, then $f(a,b)$ is maximum and it is minimum when the sign is positive. Infinitesimal variations are $\delta x = h, \delta y = k$.

Now we will apply this result to potential function $V(\emptyset_1,\emptyset_2)$ to calculate its different maxima or minima around a certain given solution.

Let us assume $\widetilde{\emptyset_1}$ &$\widetilde{\emptyset_2}$ are the solutions of eqn. (15) or (16).

If $\delta\widetilde{\emptyset_1}(=h)$& $\delta\widetilde{\emptyset_2}(=k)$ are small displacements around the point P $(\widetilde{\emptyset_1}, \widetilde{\emptyset_2})$

Then we can have$\emptyset_1 = \widetilde{\emptyset_1}$ &$\emptyset_2 = \widetilde{\emptyset_2}$ in eqn. (15) and (16).

Taylor expansion of the potential $V(\emptyset_1, \emptyset_2)$ around this solution $(\widetilde{\emptyset_1}, \widetilde{\emptyset_2})$ can be explicitly expanded as

$$V\left(\widetilde{\emptyset_1} + \delta\widetilde{\emptyset_1}, \widetilde{\emptyset_2} + \delta\widetilde{\emptyset_2}\right) = V\left(\widetilde{\emptyset_1}, \widetilde{\emptyset_2}\right) + \left[\frac{\partial V}{\partial \emptyset_1}|_{\emptyset_1=\widetilde{\emptyset_1}}\, \delta\emptyset_1 + \frac{\partial V}{\partial \emptyset_2}|_{\emptyset_2=\widetilde{\emptyset_2}}\, \delta\emptyset_2\right]$$

$$+\frac{1}{2}\left[\frac{\partial^2 V}{\partial {\emptyset_1}^2}|_{\emptyset_1=\widetilde{\emptyset_1}}(\delta\emptyset_1)^2 + \frac{\partial^2 V}{\partial {\emptyset_2}^2}|_{\emptyset_2=\widetilde{\emptyset_2}}(\delta\emptyset_2)^2 + 2\frac{\partial^2 V}{\partial\emptyset_1\partial\emptyset_2}|_{\widetilde{\emptyset_1},\widetilde{\emptyset_2}}(\delta\emptyset_1)(\delta\emptyset_2)\right]$$

$$\Rightarrow \Delta V = 0 + h^2\frac{\partial^2 V}{\partial \emptyset_1^2}|_{\emptyset_1=\widetilde{\emptyset_1}} + 2hk\frac{\partial^2 V}{\partial\emptyset_1\partial\emptyset_2}|_{\widetilde{\emptyset_1},\widetilde{\emptyset_2}} + k^2\frac{\partial^2 V}{\partial {\emptyset_2}^2}|_{\emptyset_2=\widetilde{\emptyset_2}}$$

$$= h^2\{m^2 + \lambda(3\widetilde{\emptyset_1^2} + \widetilde{\emptyset_2^2})\} + 2hk(2\lambda\widetilde{\emptyset_1}\,\widetilde{\emptyset_2}) + k^2\{m^2 + \lambda(\widetilde{\emptyset_1^2} + 3\widetilde{\emptyset_2^2})\}$$

$$= \lambda(h\widetilde{\emptyset_1} + k\widetilde{\emptyset_2})^2 > 0.$$

$\Rightarrow \Delta V > 0.$

$\Rightarrow (\widetilde{\emptyset_1}, \widetilde{\emptyset_2})$ is the solution corresponding to minimum.

This minimum is described by the following equation

$$\emptyset_1^2 + \emptyset_2^2 = \widetilde{\emptyset_1^2} + \widetilde{\emptyset_2^2} = \mu^2, where\ \mu = \sqrt{\frac{-m^2}{\lambda}} \quad (18)$$

Where, μ represents the radius of the circle/ ring made by the locus of points of which corresponds to all minima in the complex plane at a distance μ from the centre of the complex plane. It is also known as the symmetry breaking parameter for the given potential V.

Thus, for the case $m^2 < 0$ the potential is still symmetric but the minimum value of energy no longer corresponds to unique value of $\emptyset_1$&$\emptyset_2$ but instead we obtain a degenerate vacuum (I,e the minima as a ring in the complex plane defined by $\emptyset_1^2 + \emptyset_2^2 = \mu^2$)as shown in fig. (2).

Thus, in sub case **2.1**, $(m^2 > 0)$ origin $O(0,0)$ is the ground state with symmetry but in sub case **2.2**$(m^2 < 0)$ the same origin now becomes excited state and generating a new degenerate ground state giving rise to the phenomenon of SSB [7].

3. Simulation

Generated data points $(\emptyset_1, \emptyset_2)$are used in calculation of the corresponding values of the potential V($(\emptyset_1, \emptyset_2)$) and then it is plotted in gnuplot interface [**8**]. Using this platform two plots are generated corresponding to the cases $m^2 > 0$ (before SSB) as shown in fig. (3) and $m^2 < 0$ (after SSB)as plotted in fig.(4).

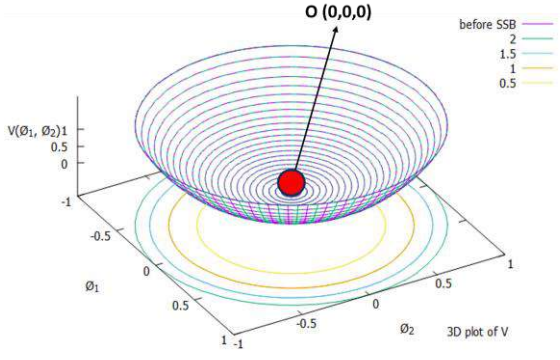

Fig. 3. 3D plot of $V(\emptyset_1, \emptyset_2)$with (0,0,0) as the base (minima) for$m^2 > 0$.

Fig. (3) is actually a paraboloid of revolution about the origin O (0,0,0). It clearly shows the symmetric nature of the plot about O. Here O

is the global minima for the given potential. When a particle is placed at O it cannot go anywhere down (local minima not available) and it always enjoys the rotational symmetry of the given potential. Fig. (4) shows an interesting symmetry pattern in which the origin O in now lifted above Z=0 plane and now it is no longer the usual global minimum position and instead a loci (ring of infinite degenerate states of radius μ) of minima is created just below Z= 0 plane. This minimum is now becomes a global minimum. When a particle chooses one of these minima (degenerate) position spontaneously, the U (1) gauge symmetry is broken and it is known as the phenomenon of *Spontaneous Symmetry Breaking* (SSB). O now becomes unstable maxima for the given field.

The geometrical shape of this potential, upon SSB, becomes similar to a "Mexican cow boy hat"and this type of Potential function is also known as "*Sombrero Potential*" or "*Higgs Potential*".

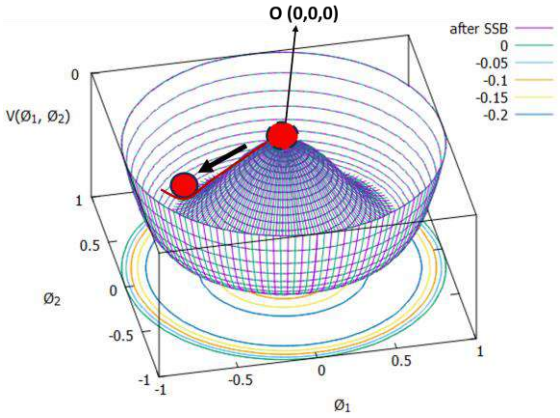

Fig. 4..3D plot of $V(\emptyset_1, \emptyset_2)$ with (0,0,0) as the base (maxima) for$m^2 < 0$.

When a particle is placed at O (as shown in Fig. 4.) it can roll down and fall in any available degenerate minima (local) and it causes SSB of the potential V. Due to this preferential behaviour of the particle the rotational symmetry is no longer available to it which it enjoyed earlier when placed at the global maxima O. So, the system remains always symmetric but the ground state ceases or break it. SSB phenomena occurs when the equation of motion (Lagrangian) satisfies certain symmetries but its ground state energy (vacuum) solutions cease to respect that symmetry, spontaneously under certain conditions. When the system goes either left or right-side lobe of the vacuum solution point $O(0,0)$of the potential as in fig. (2), the symmetry is instantly broken, but entire symmetry of the parent Lagrangian remains intact. System spontaneously transforms from symmetric to asymmetric one.

4. Conclusion

From the 3D plot in fig. (4) it is clear that when the system undergoes SSB, it has an infinite set of vacuum states, each corresponding to a point on the circumference of a circle of radius μ. Any point on the ring of minima is equivalent, as they can be obtained from any point on the circumference, by applying the condition of gauge transformation as given in eqn. (12), (13). Different ground states are orthogonal to one another. When an addition interaction terms (quartic, $\emptyset^4$ type) is added to free field potential like a small perturbation about the minima, it spontaneously causes symmetry to break in the given potential when $m^2 < 0$. This gives rise to degenerate symmetric ground states to the potential over a ring (*Mexican hat*). In this, symmetry is broken but actually it is hidden. Thus, from the above mathematical analysis, we have found several extrema values of a given potential and established whether those extrema correspond to maxima or minima. Also studied the behaviour of

potential around those inflection points w.r.t various symmetries.

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Bullying, Job Performance and other Psychological Factors among Army Personnels

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Abstract

In various professional sectors, including the military, workplace bullying, encompassing forms like verbal abuse and social isolation, adversely impacts employee performance and emotional well-being. This study explores the link between workplace bullying, job performance, stress, and emotional intelligence in the military context. Conducted on 50 army personnel aged 24-43 years, the study revealed a positive correlation between workplace bullying and job performance, however, it was also significantly positively correlated with stress, anxiety, and depression. This research emphasizes the importance of addressing workplace bullying to enhance military personnel's mental well-being.

Keywords: Workplace bullying, Army, Stress, Emotional intelligence, Job performance

Introduction

Employees' job performance doesn't just shape a company's reputation; it also impacts an individual's career and success [1]. When employees feel good about their work and are successful, they are more motivated and engaged [2]. Many things at work affect how well employees do their jobs, like job satisfaction, clear goals, and training [3]. Stress at work, including bullying, can seriously affect job performance. Bullying creates a hostile work environment, causing stress and anxiety [6]. When someone is bullied, they may feel scared and powerless, making them less productive and engaged [7], [8]. Work stress has become a big problem, with overloaded schedules and job insecurity making people feel stressed [9]. Stress can affect how well people work, sometimes in a good way, but often in a bad way [10]. Long-term stress can even cause health problems like high blood pressure and depression.

In the Indian army, work stress has led to tragic incidents. Over a thousand soldiers have committed suicide since 2003, a situation disclosed by the former Defence Minister of India, Mr A K Antony. Referring to report submitted by former Defence Minister of India Mr A K Antony to the Lok Sabha, on November 12, 2012, cited that "...suicide and fragging (to kill a fellow soldier) cases continue to remain as high as ever. Around 1,020 soldiers have committed suicide just since 2003. Disclosing the figures, Antony said while 96 soldiers had committed suicide in 2009, the figures stood at 115 in 2010, 102 (2011), and 81 till now this year"[11]. This shows how important it is for organizations to address stress and create supportive work environments for their employees' well-being.

Emotional intelligence is a vital tool in handling emotions at work. It enables individuals to understand and manage their own emotions as well as others, guiding their thoughts and actions [12]. People with high emotional intelligence can identify their feelings and use strategies to regulate them, making them better at managing stress [13]. Additionally, emotional intelligence allows individuals to adapt to the emotions of higher authorities in the workplace, aiding in effective situation management [14]. Studies have shown a strong link between emotional intelligence and stress management. Individuals with high emotional intelligence exhibit better flexibility in handling stressors [15]. This quality is particularly crucial in high-stress professions like the military, where soldiers face demanding situations both emotionally and physically [16]. By developing emotional intelligence, army personnel can effectively cope with the stressors inherent in their jobs.

In the context of the Indian Army sector, our study aims to explore the connections between workplace bullying, job performance, stress, and emotional intelligence, highlighting the importance of emotional intelligence in managing workplace challenges.

Methods

Sampling

This study followed the Purposive sampling technique. A total of 50 individuals, who were army personnel aged between 24-43 years, who were working in army for at least 2 years, and not having any known chronic psychological disorder, were drawn following purposive sampling.

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Measures

Information sheet

An information schedule was prepared for collecting the socio-demographic details like-gender, age, educational qualification, marital status, service rank/post, duration in the service, history of any psychological illness, history of any serious physical illness.

Workplace Bullying Scale (WBS)[17]

The workplace bullying scale consists of 21 items, it was used to measure bullying in workplace. The scale scored based on a five-point Likert rating scale, where 1= Never and 5 = Daily. Cronbach's alpha of WBS is 0.91.

The Individual Work Performance Scale[18]

The 18-items self-report scale was used to measure employee performance. The scale is scored by a four-point Likert rating scale, where 0= Occasionally,1= Sometimes, 2=Regularly,3= often, 4= always. The reliability coefficient for each dimension, task performance is 0.931, contextual performance is 0.904, and counterproductive work behaviour is 0.834.

Depression, Anxiety and Stress Scale - 21 Items (DASS-21)[19], [20]

The Depression, Anxiety and Stress Scale - 21 Items (DASS-21) is a set of three self-report scales designed to measure the emotional states of depression, anxiety and stress. It has four response options: 0 "Did not apply to me at all–Never", 1 "Applied to me to some degree, or some of the time–Sometimes", 2 "Applied to me to a considerable degree, or a good part of time–Often" to 3 "Applied to me very much, or most of the time–Almost always". The internal consistency reliability of the scale was 0.88 for the overall scale.

Wong and Law's Emotional Intelligence Scale(WLEIS)[21]

Consisting of 16 items to measure EI based on the revised model of Mayer and Salovey [22], [23]. The scale is composed of 16 items rated on a 7-point Likert-type scale (1 = strongly disagree, 7 = strongly agree), measuring four dimensions of Trait EI- Appraisal and expression of emotion in the self, Appraisal and recognition of emotion in others, Regulation of emotion in the self, and use of emotion to facilitate performance. Reliability coefficients as indicated by Cronbach's alpha, the reliability coefficient for the overall test was .83.

Procedure

Central Reserved Police Force (CRPF) personnels were contacted individually. Informed consents were obtained from each participant. Measures were administered in individual settings.

Result

A total of 50 participants took part in the study, with ages ranging from 24 to 43 years and a mean age of 32.30. The participants' education levels varied from 10th to 12+3 standard, with a mean education level of 11.84 years. The majority of participants were married males (86%), and there was a higher percentage of Rank-Sipahi (38%) compared to other ranks (Table 1).

Table 1. Descriptive of the participants (N=50)

Variable		Mean (SD)
Age		32.30 (5.73)
Education		11.84 (1.83)
		Frequency (%)
Marital Status	Married	43 (86)
	Unmarried	7 (14)
Ranks in CRPF	Sipahi	19 (38)
	Havildar	16 (32)
	Subedar	5 (10)
	Constable	10 (20)

Participants exhibited varying levels of stress, anxiety, and depression. Specifically, 96% of participants fell within the normal range for stress, while 50% were within the normal range for anxiety. For depression, 78% of participants were in the normal range (Table-2).

Table2. Severity on DASS for the participants (N=50)

	Level	Frequency	Percentage (%)
Stress	Normal	48	96.0
	Mild	1	2
	Severe	1	2
Anxiety	Normal	25	50
	Mild	9	18
	Moderate	15	30
	Severe	1	2
Depression	Normal	39	78
	Mild	10	20
	Extremely severe	1	2

The correlation table (Table 3) provides valuable insights into the relationships among the studied variables. Positive correlation between the

duration of service (DUR) and age, indicating that older individuals tend to have longer tenures in the army. However, this experience does not necessarily translate to better job performance (PER), as indicated by the negative correlation between job duration and performance. This implies that while experience and age increase, job performance tends to decrease. Furthermore, the table reveals a significant positive correlation between workplace bullying (WPB) and anxiety (ANX) as well as depression (DEP). This underscores the detrimental impact of workplace bullying on the mental health of army personnel, leading to higher levels of anxiety and depression. Additionally, emotional intelligence (EI) shows a negative correlation with job duration.

Table 3. Zero-order correlations among study variables.

	AGE	EDU	DUR	PER	WPB	EI	STR	ANX	DEP
AGE	1								
EDU	-.118	1							
DUR	.826**	-.191	1						
PER	-.301*	.043	-.330*	1					
WPB	-.200	.239	-.096	.298*	1				
EI	-.133	.028	-.337*	.031	-.145	1			
STR	-.106	-.030	-.044	.168	.293*	-.034	1		
ANX	-.280*	.086	-0.237	.617**	.461**	.014	.473**	1	
DEP	-.286*	.192	-.233	.324*	.349*	.059	.555**	.658**	1

Note.Edu= Education; DUR= Duration; PER=Performance; WPB= Workplace Bullying EI= Emotional Intelligence; STR= Stress; ANX= Anxiety; DEP= Depression

Discussion

The Present study aimed to investigate the association among workplace bullying, job performance, stress and emotional intelligence in Army sector. The data was obtained from the 50 army personnel.

The findings of the current study underscore a significant positive correlation between stress and workplace bullying among army personnel, indicating that bullying behaviors could be a significant source of stress within this demographic [24]. Previous research has consistently demonstrated the relationship between stress and various mental health problems, adding weight to our results [24]. Notably, our study also revealed a positive correlation between workplace bullying and depression and anxiety, aligning with existing literature highlighting the detrimental impact of workplace bullying on mental health [25]. Individuals subjected to workplace bullying often experience severe consequences, including psychological distress, burnout, and a range of mental health challenges, such as sleep disturbances, fatigue (especially in women), and diminished vigor (particularly in men) [26].

Surprisingly, our study demonstrated a positive correlation between workplace bullying and job performance among army personnel, indicating that bullying behaviors might create performance pressure, potentially leading to improved work-related outcomes, although at the expense of employees' well-being [26]. Job performance issues can stem from various factors, including low job satisfaction, inadequate remuneration, or skill deficiencies [26]. Strikingly, research from Nigeria indicated that employees perceiving lower levels of workplace bullying tend to outperform their counterparts experiencing higher levels of bullying, suggesting a complex interplay between workplace dynamics and performance outcomes [27]. However, it is crucial to note that excessive workplace bullying negatively impacts job satisfaction, potentially diminishing overall performance [28]. High job satisfaction is closely linked to enhanced performance, emphasizing the delicate balance organizations must strike to foster a productive yet supportive work environment for their employees [29].

These findings emphasize the critical need to address workplace bullying for the holistic well-being and productivity of employees within organizational settings. Surprisingly, the present study did not reveal a significant relationship between emotional intelligence and job performance, contrasting with existing academic research suggesting a notable impact of emotional intelligence on employee performance [30], [31]. Emotional intelligence's positive influence on job satisfaction has been observed in previous studies, where it aids employees in managing negative emotions while enhancing positive feelings, ultimately improving job performance [32].

Furthermore, our study indicated no direct association between emotional intelligence and stress, although extensive academic research suggests otherwise. Studies have shown that higher emotional intelligence enables individuals to cope more effectively with stress, leading to reduced stress levels [33]. However, the relationship between emotional intelligence and stress is intricate; while some studies did not find a direct correlation between overall emotional intelligence and stress, specific subscales of emotional intelligence were linked to certain stressors [33]. In the present study, we discovered a significant positive correlation between workplace bullying and anxiety and depression in the army sector, indicating the adverse impact of bullying on victims' physical and psychological well-being. This impact was further mediated by anxiety and partially by depression, highlighting the complex interplay between workplace bullying, anxiety, depression, and stress [34].

Moreover, our research shed light on the interconnectedness of anxiety and depression, revealing a mutual positive correlation. This suggests that the presence of anxiety significantly heightens the likelihood of developing depression, emphasizing the importance of addressing both conditions to foster a mentally healthy work environment [35]. Stress, acting as a predictor for both depression and anxiety, underscores its pivotal role in determining mental health outcomes [36]. These findings underscore the multifaceted nature of emotional well-being within the workplace, indicating the necessity for comprehensive strategies that address emotional intelligence, workplace bullying, stress, anxiety, and depression to promote a psychologically healthy work environment for employees.

Conclusion

In light of recent study, we can conclude that, army personnel face anxiety and depression in mild to severe range. And workplace bullying directly or indirectly inducing stress within them which may lead performance pressure, thus their job performance positively correlated with stress.

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Research Article

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Assessment Students' Performance through Principal Component Analysis and Factor Analysis: A Case Study

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Abstract

This research paper is anticipated to focus on the assessment of class 10 level students using Principal Component Analysis and Factor Analysis. Society is always expecting a high level quality of services from all the Educational Institutions. In West Bengal, there are so many Government schools, Government sponsored schools, Self-financed schools. All the schools has most dynamic curriculum. The study has been conducted to improve the academic performance of class 10 level students. Initially, we have selected one Madhyamik level school from Burdwan district in West Bengal to collect the data. Nine parameters associated with class 10 level students has been chosen. Assessment has been done using Principal component Analysis and Factor Analysis. Principal Component Analysis and Factor analysis, both are the examples of unsupervised learning method. They are also most widely used data analysis technique. In this paper, Principal Component Analysis and Factor Analysis both are used to analyse the students' parameters. A new assessment technique has also been introduced in this research paper.

Keywords: PCA, FA, Academic Performance, Students' Assessment, Parameters

Introduction

In this present scenario, class 10 level students mainly evaluated based on their performance in the examination. (pay main attention in the curriculum and pay less attention in co-curriculum and extra-curriculum activity) Here, in this work one new method has been introduced to assess class 10 level students in a different way. Therefore, this paper introduced a more comprehensive study for the assessment of class 10 level students. Principal Component Analysis and Factor Analysis, both allows us to find out the hidden pattern behind the data set. By applying Principal Component Analysis and Factor Analysis to the data set, we can increase a deeper perception into the various features that impact class 10 level students' academic achievements. By applying PCA and FA methods, the factors and more important parameters associated with class 10 level students has been identified.

Data Collection

Data has been collected from Belar-Bhurkunda High School, a Madhyamik school in Burdwan district of West Bengal. Details of 25 students in 2011 Madhyamik batch and 25 students of 2012 Madhyamik batch has been selected randomly. Nine parameters has been chosen, they are (x1) Attendance in School, (x2) Discipline in school, (x3) Result in different class test, (x4) Result in different surprise test, (x5) Financial background, (x6) Communication skill,(x7) Comprehensive skill, (x8) Professional skill, (x9) Dress code and the Total Marks.

Methodology:

Principal component analysis (PCA) is one example of Unsupervised Learning Method. Although it is oldest technique, but most widely used multivariate data analysis. It was first introduced by Pearson in 1901, and developed by Hotelling in 1933. It is applied in economic and statistical research. It is a method for dimension reduction and feature extraction. By applying Principal Component Analysis, the weights of Principal Components are automatically generated. Therefore, Principal Component Analysis is a more powerful tool for feature extraction.

Factor Analysis is also most widely used statistical tool for multivariate data analysis. By applying Factor Analysis, we will be able to find the factors from a huge number of variables. It has some unique features. Factor Analysis is performed on continuous variables and categorical variables. Generally, Factor Analysis has two types, EFA (Exploratory Factor Analysis) and CFA (Confirmatory Factor Analysis).

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Principal Component Analysis and Factor Analysis has implemented by using R programming language. R is open source programming language used for data analysis. It is also the leading tool for Machine Learning, Statistics etc.

Table 1.

Index	X1	X2	X3	X4	X5	X6	X7	X8	X9	Total Marks in class 10 Examination (800)
1	9	8	9	6	5	6	7	8	7	555
2	9	9	9	7	4	9	9	9	8	480
3	8	8	8	6	8	6	8	7	7	434
4	9	9	8	7	9	7	7	7	7	480
5	7	9	8	7	7	7	7	7	9	480
6	8	8	8	6	9	7	7	8	7	320
7	7	8	8	7	4	7	8	7	8	375
8	8	7	7	6	7	6	7	8	7	359
9	8	8	7	7	5	8	7	8	7	301
10	7	7	8	6	5	7	8	7	8	327
11	8	8	7	7	4	7	8	7	7	311
12	8	7	8	6	4	8	7	8	7	274
13	8	8	7	7	4	7	7	8	8	324
14	7	7	8	6	7	6	8	7	8	270
15	8	8	7	7	4	7	7	8	8	273
16	9	9	9	9	8	9	9	9	9	715
17	9	9	9	9	7	8	8	9	9	633
18	9	8	8	8	8	8	8	8	9	630
19	8	8	8	8	7	7	8	8	7	491
20	8	8	7	7	6	8	8	7	8	482
21	8	7	7	8	6	7	8	8	7	500
22	7	7	7	6	7	7	7	7	7	338
23	7	7	7	7	4	8	8	7	7	392
24	8	8	8	7	8	8	8	7	8	387
25	7	7	7	8	7	7	7	8	7	305
26	8	7	8	8	4	8	8	9	9	282
27	8	9	9	9	8	8	9	9	9	493
28	8	8	8	8	7	7	8	8	8	348
29	9	9	9	9	4	9	9	9	9	420
30	9	9	8	9	4	8	8	8	8	420
31	8	9	9	9	9	9	8	7	8	522
32	8	8	8	7	4	7	7	7	7	261
33	8	8	8	8	7	8	8	8	8	377
34	8	8	8	8	5	8	8	8	8	376
35	8	7	7	8	7	8	8	7	8	236
36	9	9	9	9	4	8	8	8	8	233
37	8	8	7	7	4	7	7	8	7	324
38	8	8	8	8	4	8	8	7	7	211
39	9	9	9	9	7	8	8	8	8	379
40	7	7	8	7	4	8	8	7	7	233
41	9	9	9	9	9	9	9	9	9	422
42	9	9	8	8	8	8	8	8	8	229
43	8	8	7	7	4	8	8	8	8	276
44	8	8	8	8	8	8	8	8	8	377
45	8	7	7	7	7	7	8	8	8	270
46	9	9	9	9	6	8	9	9	9	383
47	8	8	8	8	4	8	8	7	7	235
48	9	9	9	9	4	8	8	9	9	360
49	8	8	8	8	7	8	8	7	7	238
50	7	7	7	7	4	7	7	7	7	208

Principal Component Analysis

Step 1: Data has been stored in Table-1.

Step 2: Correlation matrix of Table-1 has been calculated and stored in Table-2.

Table-2:

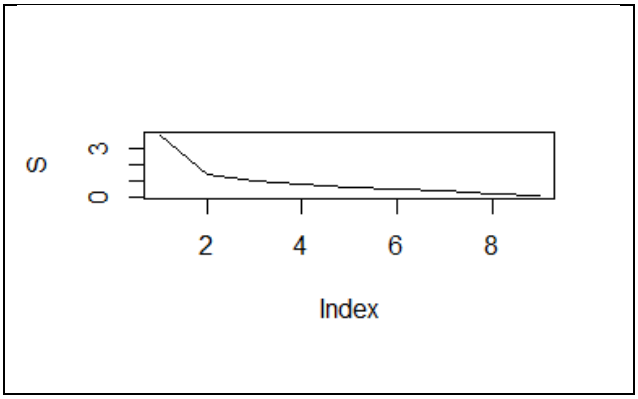
INDEX	C1	C2	C3	C4	C5	C6	C7	C8	C9
1	1.00000	0.6156731	0.5452753	0.3726780	0.21305422	0.2740243	0.23473428	0.6188525 7	0.1976934
2	0.6156731	1.00000	0.6008521	0.4402603	0.23497170	0.2946789	0.26289626	0.3215206 5	0.5247148
3	0.5452753	0.6008521	1.00000	0.1936492	0.19038649	0.1545288	0.38809117	0.4377327 7	0.4822493 9
4	0.3726780	0.4402603	0.1936492	1.00000	0.16385860	0.4274910	0.42948745	0.5216405 3	0.4822428
5	0.2130542	0.2349717	0.1903865	0.1638586	1.00000	-0.1662474	-0.0969526 7	-0.0170950 6	0.1488203
6	0.2740243	0.2946789	0.1545288	0.4274910	-0.1662474 3	1.00000	0.51648711	0.4705228 7	0.2803701
7	0.2347343	0.2628963	0.3880912	0.4294487	-0.0969526 7	0.5164871	1.00000	0.2576205 6	0.4107455
8	0.6188525	0.3215206	0.4377327	0.5216405	-0.0170950 6	0.4705229	0.2576205 6	1.00000	0.4107455
9	0.1976934	0.5247148	0.4822493	0.4822428	0.1488203	0.2803701	0.4107455	0.4107455	1.0000

Step 2: The Eigenvalues, Variance Contribution rate, % of variance, cumulative % of variance of Table-1 has been fitted out in Table-3.

Table-3:

Eigenvalues	Variation Contribution Rate
3.7831200	0.4203466667
1.4389563	0.1598840333
1.0522145	0.1169127222
0.8611653	0.0956850333
0.5842439	0.0649159889
0.5089683	0.0565520333
0.4177129	0.0464125444
0.2314381	0.0257153444
0.1221808	0.0135756444

Step-3**:** Eigenvalues has been plotted in a graph, and observed more important parameters related to class 10 level students.



Step-4: Eigenvectors of Table-2 has also been furnished in Table-4.

Table-4

INDICATORS	C1	C2	C3	C4	C5	C6	C7	C8	C9
X1	-0.3743 8782	-0.2230 7603	-0.4778 6487	-0.0072 7861 6	-0.0082 5710 5	0.1658 9158	0.3040 1777	0.6181 6341 2	-0.2598 6044
X2	-0.3935 2403	-0.2740 3039	0.0720 1657	-0.1397 0610	0.3166 0947	0.5594 7983	0.2114 965	-0.3334 2313	0.4197 3923
X3	-0.3651 8111	-0.2719 6947	0.0176 8917	-0.5471 1595	-0.1576 3384	-0.2793 3363	-0.1956 4435	-0.4029 3946	-0.4353 3271
X4	-0.3634 7310	0.1413 7375	0.1032 2454	0.5928 8844	0.2284 5344	-0.2165 3652	0.3984 0073	-0.2871 5186	-0.3813 9649
X5	-0.0951 9851	-0.6123 8317	0.1524 7916	0.5099 679	-0.5014 9773	0.0405 4505	-0.2611 432	-0.0056 6031 1	0.1058 5744
X6	-0.3014 41	0.4989 098	-0.0548 700	0.1383 1542	-0.1638 9	0.5256 7061	-0.5236 0	-0.0365 46	-0.2436 944
	31	5	0		524		90	359	6
X7	-0.3113 4450	0.3702 985	0.3319 8462	-0.1681 7353	-0.6072 5302	-0.1147 770	0.3827 4717	0.0717 8626 5	0.3076 8549
X8	-0.3597 0523	0.1337 3265	-0.5296 8247	0.1216 6414	0.0892 5797	-0.4534 2596	-0.2909 0964	-0.0766 9429 3	0.5037 4796
X9	-0.3365 2606	-0.0048 0806 2	0.5817 6683	-0.0044 9381 6	0.4010 1898	-0.1963 4434	-0.3046 7677	0.4994 8174 0	0.0478 3849

Factor Analysis:

Step 1: Evaluation of Data. (Correlation Matrix, KMO)
Step 2: Factor Extraction. (PCA)
Step 3: Eigenvalues, Variance Explained.
Step 4: New Constructs.

Conclusion

Principal Component Analysis and Factor Analysis both are used for dimensionality reduction, i.e. higher dimension to lower dimension. In this research work, Principal Component Analysis has been implemented to find more and less important features related to class 10 level students. Factor Analysis has been implemented to find the factors related to class 10 level students. In case of PCA more important attributes are equal to the number of original variables, and in case of Factor Analysis, the factors are equal to the original variables. The steps of PCA and FA, are almost same. We only can differentiate them in terms of their applications. The future researchers of this domain can apply both PCA and FA for education systems assessment.

In this research work, it has been shown that first two components are most correlated with the indicators “Result in Surprise Test” and “Financial Background” respectively. So we can conclude by applying Principal Component analysis these two are more important parameters to assess class 10 level students. It has also been shown that by applying Factor Analysis we will find two

factors among nine components for class 10 level students assessment.
Our main aim was to identify the class 10 level students, those has the ability to improve their academic performance, but they won't be able to implement due to several reasons. The idea of this paper is also be helpful for the future researchers of this domain.
Based on the primary data, this research paper attains a complete evaluation methods of class 10 level students quality. By calculating the scores of Principal Components and find Factors, we can observe the strengths and weaknesses of class 10 level students.

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Review Article

Study of Non-Enzymatic Antioxidant Activity of Apocynaceous Plant Species, Available from Purulia District, West Bengal, India: A Review

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Abstract

Reactive oxygen species (ROS) are activated derivatives of oxygen, formed by incomplete reduction of molecular oxygen due to redox imbalance. ROS play a harmful role to cellular damage and pushes us towards severe oxidative stress-related diseases, like cancer, liver injury, lung damage, cardiovascular disorders, inflammation etc. Plants are natural source of antioxidant, the scavenger that remove injurious free radicals and combat detrimental diseases. The present study deals with the significance of Apocynaceae (Dogbane) family, with special reference to understanding of more effective and less toxic non enzymatic antioxidant type bioactive compounds which may be resistant to oxidative stress and improve healthcare system of human being. Many species of Apocynaceae having novel phytochemical compounds earned worldwide reputation as a source of life-saving drugs. In this review collection of detailed information, data collection and evaluation of natural antioxidant property, were done from various literature sources wherein data were generated by the methods like widely used assay, DPPH (1,1-diphenyl 2- picryl hydrazyl), ABTS etc. Phenols, carotenes, xanthophylls, sterols, different alkaloids, glycosides, saponins etc. exhibited potential non-enzymatic antioxidant capacity. In this comprehensive study, non-enzyme antioxidant profile of 29 plants species under Apocynaceae family from Purulia district of West Bengal is represented.

Key words: Non-enzymatic antioxidants, Reactive oxygen species, Oxidative stress, Apocynaceae

1. Introduction

Medicinal plants with their bioactive phytochemicals play protective role by defending free radicals generated after normal metabolic processes in the body with their antioxidant potential.

Normally believed that plant-based natural medications are pure, healthier, non-toxic and inexpensive than artificial synthetic drugs for human being in modern culture. Indian system of medicine like Ayurveda predominantly uses plants as source of drugs or formulation of drugs to cure various critical diseases because they contain bio-active constituents with therapeutic properties. Phytochemicals are synthesized as secondary metabolites which are found in minor amount in higher plants. The term “antioxidant” refers to any substance that delays, prevents or removes oxidative damage to a target molecule[1]. Medicinal plants possess natural antioxidants such as steroids, phenols, polyphenols, flavonoids, carotenoids, alkaloids, tannins, terpenoids, ascorbic acid (AA), reduced glutathione (GSH), other thiol compounds, alpha tocopherol, proline etc. Antioxidant plays significant role in removal of reactive oxygen species (ROS), thus fight against harmful infections and detrimental effects of cells in different stress conditions. They also prevent various pathological diseases and other life-threatening ailments such as cancer, cardiovascular and neurodegenerative diseases which are believed to be associated with oxidative stress[2]. In recent decades, interestingly natural antioxidants like flavonoids, anthocyanins, essential oils etc. not only cause health promotion but also used in cosmetics because they are nontoxic and eco-friendly than artificial antioxidants. Numerous natural antioxidants have already been isolated from different varieties of plant material such as leafy vegetables, fruits, seeds, cereals and algae[3].

Oxidative stress:

In the cellular environment presence of oxygen causes a constant oxidative threat to cellular biochemical processes and structures[4].Oxidative stress is induced due to free radicals generated during oxidative breakdown of our food to simpler forms [5].It is well established that redox imbalance or highly oxidizing metabolic activities are the key source of Reactive Oxygen Species (ROS). ROS leads to an increased membrane lipid peroxidation and cause injury to cell and also attack on cell protein, lipids and DNA[6]. This destructive situation leads to oxidative stress.

Chemistry of ROS:

Mitochondria, peroxisomes of all cells and chloroplast in photosynthetic cells are major organelles for producing ROS. During cellular respiration in mitochondria and photosynthesis in chloroplast, due to unwanted extreme rate of

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electron flow through Electron Transport Chain (ETC) and Z-scheme respectively, causing redox imbalance. Atmospheric molecular oxygen is relatively non-reactive. But, in adverse situation under redox imbalance conditions, at the end of electron flow chain electrons are partially accepted by last electron acceptor, the oxygen and this leads to formation of ROS. ROS both comprise free radical form, superoxide radical(O_2^-), hydroxy radical (OH), perhydroxy radical (HO_2-), alkoxy radical (RO^-), peroxy radical (ROO^-) and non-radical form hydrogen peroxide(H_2O_2), singlet and oxygen ($^1O_2$). Reactive oxygen species like OH, HO_2^-, H_2O_2, $^1O_2$, O_2^-, H_2O_2 etc play a key role for oxidative damage of cells. The univalent reduction of O_2^- produces hydrogen peroxide (H_2O_2), which is moderately reactive. Singlet oxygen ($^1O_2$) is an unusual ROS, not related to electron accept by oxygen. Other exclusive sources of ROS production within cells are causal agents for detoxification reactions catalysed by cytochrome p450 in cytoplasm and endoplasmic reticulum (ER). ROS are also generated at plasma membrane level or extracellularly in apoplast in plants. pH-dependent cell wall-peroxidases, germin-like oxalate oxidases and amine oxidases have been proposed as a source of H_2O_2 in apoplast of plant cells [7]. Thus, ROS are highly toxic, cause lipid peroxidation (LPO), protein oxidation, damage DNA, carbohydrates etc. and at last cell death resulted.

Antioxidants: The scavengers of ROS

A great deal of research has established that the induction of the cellular antioxidant machinery is important for protection against various cellular damages. The components of antioxidant defence system are enzymatic and non-enzymatic antioxidants. Enzymatic antioxidants include superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), monodehydro ascorbate reductase (MDHAR), dehydroascorbatereductase (DHAR), guaiacol peroxidase (GPOX), and glutathione S-transferases (GST). Non-enzymatic antioxidants are glutathione (GSH), ascorbic acid (vitamin C) (both water soluble), carotenoids, α-tocopherols (vitamin E, lipid soluble)[8]. Other antioxidant molecules like carotenoids (β-carotene), flavonoids, phenolics, polyphenols, proline etc. These are playing a key role in scavenging free radicals in cells by donating electron or hydrogen [9].

Apocynaceae:

Apocynaceae, the largest angiosperm family commonly known as the Dogbane (Gentianales), most of the species are characterised by producing white milky latex often having poisonous juice or exudates. The expanded family includes five sub-families of Apocynoideae, Asclepiadoideae, Periplocoideae, Rauvolfioideae and Secamonoideae[10]and this new largest comprises 375 genera and 5100 species[11]. Plants of family Apocynaceae are usually distributed in tropical and subtropical regions with herbs, shrubs, sub shrubs, vines, succulents, and trees [12]. About 44 genera and 145 species of Apocynaceae have been reported from China, among them 95% are found in the southern and south western regions of China and of which one genus with 38 species are endemic[13]. In India from different regions several indigenous communities use Apocynaceae plants for medicinal or other purposes like food, fodder, timber, ornamental, perfume, dyes, poison, etc.[14]. Apocynaceae is known as a medicinally important family and species are rich in toxic and medicinal secondary metabolites such as alkaloids, triterpenoids, flavonoids, glycosides, phenols, steroids, lactones, and sterols [15],[16],[17]. Many crucial drugs from this family like cardiac glycosides are highly effective in heart functioning[18] and thus, many apocynaceous plants are potent source of antioxidants.

However, a comprehensive review work on ethnomedicinal plants, particularly from Apocynaceae family species of Purulia district, West Bengal with their antioxidant activities is not available. Hence, the main objective of the present review is accumulation of detailed information and evaluate efficacy of Apocynaceae plant species with reference to their antioxidant properties, from Purulia district, West Bengal.

3.Methodology:

A total 29 species of the Apocynaceae family were selected for the present review with prime focus on preparation of non-enzymatic antioxidant profile. The species are available in several tribal regions of the Purulia district, West Bengal. By using search engines such as Google, Yahoo etc. 18 species of this family have already been reported time to time from different areas of Purulia district by several researchers. About eleven tribal communities throughout the Purulia district are using the whole plants or parts of the plants like root, leaf, bark, flowers etc for curing many health problems. Information on the ethno-medicinal plants and their antioxidant activities have been collated from various sources including journals, books, scientific databases, floras, eFloras, websites like PubMed, Embase, Google Scholar, Scopus, Science etc. Accepted scientific names, synonyms and antioxidant activities of the selected 29 species are illustrated at 'Results and Discussion' section along with references. Accepted botanical names and their synonyms have been confirmed from The Plant List.org (TPL, 2013).

Determination of Antioxidant Activities:

The antioxidant potential of the methanolic plant extract is determined on the basis of their scavenging activities of the stable 1,1-diphenyl 2-picrylhydrazyl (DPPH) free radical. DPPH method

is most widely used and easiest method to determine antioxidant activity (20). Due to the presence of free radical scavenger an odd electron gets combined with an antioxidant agent, DPPH radicals get concentrated to corresponding hydrazine, DPPH-H form, and the sample solution changes from deep violet to light yellow colour [19]. UV spectrophotometer is used for measuring of absorbance and ascorbic acid is used as a reference standard [20].
DPPH inhibitory effect is calculated according to the following formula:

$$\% \text{ inhibition} = \frac{(\text{Absorbance of control} - \text{Absorbance of test sample}) \times 100}{\text{Absorbance of control}}$$

The antioxidant activity of each sample is expressed in terms of IC50. (µg/ml) concentration required to inhibit DPPH radical formation by 50% [20]. Another test for antioxidant activity analysis are metal ion chelating, hydrogen peroxide scavenging, superoxide anion radical scavenging, and ferric thiocyanate reducing ability, are compared to standard antioxidants such as butylatedhydroxyanisole (BHA), butylatedhydroxy toluene (BHT), l- ascorbic acid and α-tocopherol[21].

4. Result and Discussion

Antioxidant capacity and diversity of antioxidant, compounds of 29 different species of Apocynaceae was studied and discussed (Table 1). Information and data from search engines and e-resources revealed that all 29 species possess more or less level of antioxidant property, due to presence of various bioactive compounds. Comparison of antioxidant capacity, based on DPPH assay of non-enzymatic antioxidants in **table 1**. Results showed that, out of 29 species, 13 species has high (H), 7 species moderate (M), 5 species low (L) antioxidant activity. A brief account of species-wise nonenzymatic antioxidants is given hereunder. **I.*Allamanda blanchetii* A.DC.:**
Flowers of purple allamanda has higher amounts of flavonoids, polyphenols, polysaccharide [22]. Two active compounds such as plumericinisoplumericin and 5,6-dimethoxycoumarin (unckalin) are detected from this plant. The floral extracts exhibited comparatively higher anti-oxidant property[22]than other plant parts and different extractions have free radical scavenging potential with IC50 values ranging from 40.50 to 119.21 mg/ml. The highest free radical scavenging activity was demonstrated by the carbon tetrachloride soluble fraction. A positive correlation was seen between total phenolic content and total antioxidant activity [23].
II.*Allamanda cathartica* L.:
Numerous phytochemical investigations of plants from the *A. cathartica* (also called golden trumpet or yellow allamanda) have shown the presence of hydrocarbons, alcohols, esters, ethers, aldehydes, ketones, fatty acids, phospholipids, volatile compounds, phenolic compounds, flavonoids, alkaloids, steroids, terpenes, lactones, and carbohydrates [24]. Flowers of this plant has higher amounts of flavonoids, polyphenols, polysaccharide [22]. In DPPH assay, as compared to standard antioxidant ascorbic acid, methanolic extract of this plant showed mild antioxidant activity [25]. The floral extracts display comparatively higher anti-oxidant property [22].
III.*Allamanda schottii* Pohl:
This plant is commonly known as bush allamanda. The active components, in order of elution on Sigel, are: isoplumericin, plumericin, scoparone, allamandin, scopoletin, pinoresinol, and allamcin[26]. Phytochemical screening result showed the presence of saponin, terpenoids, flavonoid, tannin and alkaloid with antioxidant activity [27].
IV.*Alstonia scholaris* (L.) R.Br.:
*Alstonia scholaris*is popularly known as "Saptaparni" or "Devil's tree". When cut, the outer blaze is cream to yellow with abundant, milky latex. Qualitative phytochemical screening revealed the presence of alkaloids, glycosides, flavonoids, saponins, triterpenoids, tannin, gums and mucilage as well as oils and fats in bark, stem and leaf extracts. Quantitative tests revealed that glycosides, alkaloids, gums and mucilage are present in higher quantity in bark but not in leaf and stem[21], [28]. In DPPH method, ethanolic leaf extract (1mg/mL) shows 63% of inhibition as compared to standard antioxidant ascorbic acid [21]. Both aqueous as well as methanol extracts from bark showed potent total antioxidant activity. Particularly at higher concentrations (200, 250 and 300 µg/ml), the antioxidant activity of aqueous extract was higher than that of standard Ascorbic acid [28].
V.*Calotropis gigantea* (L.) Dryand.:
Calotropis gigantea, the crown flower locally known as akanda, with waxy flowers having lavender colour. Preliminary phytochemical screening showed the presence of alkaloids, sterols, triterpenes, saponins, flavonoids, tannins, carbohydrates, cardiac glycosides and amino acids [29]. Ethanolic extract of leaves (1mg/mL) showed 67.90% [30] and methanolic extract of leaves 400µg/mL concentration showed maximum DPPH radical scavenging activity showing 85.17% of inhibition as compared to standard antioxidant ascorbic acid[29]. In comparison to that of ascorbic acid, the free radical scavenging activity exhibited by the extract was concentration dependent. This activity of the extract is mainly due to the presence of flavonoids and terpenoids[31].
VI.*Calotropis procera*(Aiton) W.T. Aiton:
Commonly known as 'apple of sodom' or rubber bush, this plant is characterised by presence of

poisonous milky sap. Phytochemical analyses of its latex revealed that it possesses antioxidants, namely terpenes, phenolic compounds and cardenolides, flavonoids, saponins, glycosides, tannins, phytosterols, acetogenins. Latex also contains enzymatic antioxidants, namely superoxide dismutase (SOD), catalase and glutathione [32]. Ethanolic leave extracts show highest free-radical scavenging activity, 84.23 % inhibition of DPPH radical [33]. In another report, methanolic leaf extract (10mg/ml) showed75.00 % inhibition as compared to ascorbic acid [34]. Methanol extracts of the leaves of exhibit strong antioxidant activity, while the aqueous extract showed mild antioxidant activity [35].

VII.*Carissa carandas* L.:

Common name 'Bengal currant' or 'Christ's thorn', having berry like fruits commonly used as a condiment in Indian pickles and spices. The fruit extract was orange-pink, translucent, and used in toner formulation[36]. Its fruits contain a high amount of antioxidant substances such as anthocyanin and vitamin C. Phenolics in ripe fruit, for example, isoamyl alcohol, benzyl acetate, lupeol, oxalic acid, tartaric acid, citric acid, malic acid, malonic acid, and glycolic acids, also exhibited antioxidant activity [36]. The inhibition concentration (IC50) of *Carissa carandas* was found to be 27.45±0.43µg/ml. The therapeutic value of a plant mainly depends upon its antioxidative property. Certain compounds like ascorbic acid, phenolics, carotenoids, tocopherol etc. can enhance antioxidant activity. Phenolic compounds and ascorbic acid contribute greatly to the antioxidant activity of a fruit[37]. By using DPPH assay, the lyophilized fruit extract exhibited antioxidant capacities with the inhibitory concentration (IC50) value of 633.42 ± 0.64 µg/ml. [36]. Methanolic extract of leaves was found to exhibit significant dose-dependent DPPH radical scavenging, total antioxidant activity (IC50 value= 73.12µg/ml).

VIII.*Carissa spinarum* L:

*Carissa spinarum*is known as 'conkerberry' or 'bush plum'. The phytochemical screening of extract showed the presence of various phytoconstituents like alkaloids, glycosides, tannins, protein, phenols and flavonoids [38]. In DPPH assay methanolic extract showed stronger antioxidant activity, 56.314±0.639% inhibition as compared to ascorbic acid [38].

IX.*Catharanthus roseus* (L.) G.Don:

Catharanthus roseus (L.) G. Don was previously known as *Vincarosea*(L.) and commonly known as Madagascar periwinkle. This is an ornamental shrub that grows up to30–100 cm in height. By using eutectic solvent solution, *Catharanthus roseus* plant parts, particularly flower petals, showed higher total phenolic content, than root and stem, and leaves have the lowest total phenolic content [19]. Several other reports revealed that plant has various compounds, like terpenoidalindole alkaloids, vinca alkaloids, flavonol glycosides, anthocynidin glycosides and simple phenolics. By DPPH method and using eutectic solvent solution, *Catharanthus roseus* root, stem, leaves, and flower petal was found to contain differential antioxidant activities. The per-centage inhibition of *Catharanthus roseus* plant parts, flower petal, root, stem, and leaves, were detected 73.13 68.64, 64.87, and 61.16%, respectively as compared to ascorbic acid, the standard antioxidant. Flower petal showed highest antioxidant activity. It is concluded that to this plant has strong antioxidant activity it would be an amazing source of beneficial antioxidants that can be helpful for the treatment of diseases caused by free-radical oxidative stress[19].

X.*Catharanthus pusillus* (Murray) G. Don:

Commonly known as the tiny periwinkle and local name sadabahar, marchiara. Terponoid indole alkaloids are predominant in this plant. This species seems to constitute a precious source of the monomerics, vindoline and catharanthine, intermediates in the synthesis of the two important antitumor dimerics vincristine and vinblastine [40].

XI.*Cryptolepis dubia* (Burm.f.) M.R.Almeida .:

Local names are Dudhia, dudhlalar. having activities of enzymatic antioxidant like SOD, CAT, LP, GSH and GPX [41],—but non-enzymatic antioxidant activity yet not reported.

XII.*Gymnema sylvestre*(Retz.) R. Br. ex Schult:

Vernacular name is merasingi and hindi name is 'gurmar' means sugar destroyer. Leaves reduce sensitivity to sweet substances after chewing. Leaves contain lupeol, β-amyrin, stigmasterol, pentriacontane, hentricontane, α and β chlorophyll, resin, tartaric acid, gymnemic acid, anthraquinone derivatives, alkaloids, betaine choline and trimethylamine. Antisweet constituent of the leaves has been found to be a mixture of triterpenesaponins. The sugar residues are glucuronic acid and galacturonic acid while ferulic and angelic acids have been attached as the carboxylic acid. Methanolic leaf extract revealed the presence of some active ingredients such as alkaloids, cardiac glycosides, tannins, saponins, anthroquinones, phenols and flavonoids [39]. Methanolic extract of the leaves showed good DPPH scavenging activity. At higher concentrations its radical quenching ability was identical to the standard ascorbic acid. Ethanolic leaf extract showed highest DPPH radical scavenging activity with 83.41±0.13% at 120 µg/ml concentration (which is nearly close to the value of Ascorbic acid a standard antioxidant) [39]. The activity found for methanolic extract at its highest concentration of 6 µg was 82.5% [40].

XIII.*Hemidesmus indicus* (L.) R. Br. ex Schult:

This plant has different local names like Huringonal, anantamul, marangonol sing dhubi, having prostrate or semi erect shrub habit. The phytochemical screening of the ethanolic extract (yield, 9.2%) of root was dark brown in colour and sticky in nature indicating positive results for having flavonoids, terpenoids, tannins, coumarins, glycosides, polyphenols and coumarins. Alkaloids are not found in the extract i.e., negative results for alkaloids, anthraquinones, lactones/ester, protein/ amino acids, and saponins [44, 45]. The methanolic extract of *H. indicus* root bark exhibited different levels of antioxidant activity in all the models studied. It showed a concentration dependent antiradical activity by inhibiting DPPH radical with an EC50 value of 18.87 µg/ml [41].

XIV.*Holarrhena pubescens Wall.ex G.Don:*

The vernacular name is Kurchi, tuar, indrajob and presence of flavonoides, phenolic compounds suggested that they possess a number of common antioxidants [42]. In several reports, extract of bark has compounds like non-alkaloidal constituents kurchinin, kurchinicin, holarrheno and alkaloids holamine, kurchamine, holaphyllidine, holaromine, mitiphylline, holadysenterine[43]. The methanolic and water extract showed strong antioxidant activity with inhibition of more than 90% DPPH free radicals at the concentration of 100µg/mL [42].

XV.*Holostemma annularis* K.Schum:

Commonly known as jivanthi, this plant yields terpenoid sugar and other highly valued secondary metabolites, which have antioxidant property. Plant extracts exhibited significant dose-dependent DPPH radical scavenging activity, with a 50% inhibition (IC50) at a concentration of 265.95, 151.51and 68.18µg/ml respectively. The IC50 value of the hexane and ethyl acetate extract was found to be lesser than the standards [49].

XVI.*Ichnocarpus frutescens* (L.) W.T. Aiton*:*

Commonly known as 'black creeper', with several vernacular names like Pirihore, onol sing, chotodudhi, dudhilata, shyamalata, dugdhalata, sayalata, perilata. Phytochemical analyses revealed the presence of flavonoids, polyphenols, anthocyanins and simple phenolic acids. Various solvent extracts of the plant have been reported to be potent free radical scavengers and inhibitors of lipid peroxidation [44]. The percentage inhibition of 40 µg/ml concentration of methanolic extract in DPPH radical scavenging model was found as 86.7% [45].

XVII.*Nerium indicum* Mill.:

Local name is 'raktakarabi'. All the extracts have been found to contain significant amount of total flavonoid and phenolic compounds. Both of these compounds have good antioxidant potential and their effects on health and disease prevention are considerable. Flavonoids are polyphenolic plant secondary metabolite characterized by a common benzopyrone ring which functions primarily as antioxidants and also have cardio protective role[46]. The methanolic extracts of leaf, stem and root of showed excellent dose-dependent scavenging activity of DPPH radical. The IC50 values of the leaf, stem and root extracts and standard ascorbic acid were 217.15 ± 18.39 ìg/ml, 63.56 ± 1.63 ìg/ml, 166.18 ± 6.84 ìg/ml and 5.29 ± 0.28 ìg/ml respectively. At 100 ìg/ml, the percentage of inhibition of the leaf, stem and root extracts were 33.14%, 64.16% and 38.03% whereas at 45 ìg/ml the standard ascorbic acid shows 27.93% inhibition[46].

XVIII.*Nerium oleander* L.:

Historically considered as poisonous plant having a local name karabi. Various compounds have been reported in connection with these biological activities, such as cardenolides (oleanderin, neriantin, adynerin, deacetyloleanerin, neriifolin), triterpenoidalsaponins, oleanderol, rutin, dambonitol in leaves; odorosides (A, B, D, F, G, H, K) in barks; triterpene, steroidal cardenolide, volatile oil, stearic acid, oleic acid in roots; and gitoxigenin, uzarigenin, strospeside, odoroside H in flowers [47]. Methanolic extract contained highest amounts of phenolic compounds and exhibited the maximum antioxidant activity. The *in vitro* DPPH assay showed high scavenging property of methanolic extract 78.52±0.37, may be due to hydroxyl groups existing in the phenolic compounds, chemical structure that can provide the necessary component as a radical scavenger [20].

XIX.*Pergulariadaemia* (Forsk.) Chiov.:

The trellis vine and local name is latabakanda. The phytosterols, saponins, phenols, alkaloids, tannins, flavonoids and triterpenes found in the extract may be responsible for the observed anti-hyperglycaemia and antioxidant activities [48]. In the DPPH radical scavenging assay, the extract showed a concentration dependent radical scavenging effect. In this assay, the lower the EC50 values the higher the ability to scavenge for oxygen radicals. In comparison to ascorbic acid and BHT, the extract had a lower scavenging effect. The EC50 values were 2.608, 0.149 and 0.699mg/mL for the extract, ascorbic acid and BHT, respectively [48].

XX.*Plumeria acutifolia* Poir.:

Plumeria acutifolia is an ornamental plant, with long, oval and pointed leaves. Plant used in the traditional medicine and known to have a variety of constituents as alkaloids, flavonoids, and iridoids[49]. The antioxidant activity was concentration dependent; ethyl acetate fraction showed the most predominant effect, with an IC50 of 197.1 µg/ml and inhibition with 82.81%. Five compounds were identified as narcissinquercitrin, sweroside, gaertneroside and plumieride[49].

XXI.*Plumeria obtusa* L.:

Singapore graveyard flower, leaves are ovate or teardrop shaped. Various phytochemicals like alkaloids, flavonoids, terpenoids, glycosides and

sterols are present, which show antioxidant activity. Methanolic extract of leaves has antioxidant inhibitory effect, 38.12±0.641 as compared to ascorbic acid [50].

XXII.*Plumeria rubra* L.:

Common name fringipani and local names are Lalgorur, gulach, Plant has antioxidant and hypolipidemic activity due to presence of flavone glycoside compounds[51]. More than 110 chemical constituents have been isolated from *P. rubra* including iridoids, terpenoids, flavonoids and flavonoid glycosides, alkaloids, glycosides, fatty acid esters, carbohydrates, animo acids, lignan, coumarin, volatile oils, etc. The important chemical constituents responsible for pharmacological activities of the plant are fulvoplumierin, plumieride, rubrinol, lupeol, oleanolic acid, stigmasterol, taraxasteryl acetate, plumieride-p-*E*-coumarate, rubranonoside, rubrajalellol, plumericin, isoplumericin, etc. The plant possesses a wide range of pharmacological activities present namely antibacterial, antiviral, anti-inflammatory, antipyretic, antidiabetic, hepatoprotective, anticancer, anthelmintic, antifertility and many other activities [52].. Highest antioxidant activity was found in *P. rubra* flowers[51]. Plant latexes (58±2.9%) also possess good antioxidant activity [53].

XXIII.*Rauvolfia serpentina*(L.) Benth. exKurz:

This plant is commonly known as "quinine tree" with local name 'Chotachand', 'sarpagandha'. *Rauvolfia* is important from a medicinal point of view because of the presence of N-containing indole alkaloids, which are localised in roots [54]. Nutrients and phytochemical characterisation included determination of tocopherols by HPLC-fluorescence, phenolics, flavonoids, carotenoids, ascorbic acid and pigment composition by spectrophotometric techniques. *Rauvolfia serpentina* exhibited the highest total phenolic content [55]. DPPH assay showed a percentage inhibition of 19, 27.5, 38, 47.9, and 55 for cultivated and 34.99, 62.5, 76.09, 81.94, and 84.64 for wild at 0.1, 0.2, 0.3, 0.4, and 0.5 µg/ml concentrations, respectively. The DPPH radical scavenging activities of the species of *Rauvolfia* leaf extracts increased with increasing concentrations [60]. At 100 g/mL, the highest DPPH radical scavenging activity (93.1 ± 0.06%) was observed in *R. serpentina* than R. *tetraphylla*[55].

XXIV.*Rauwolfia tetraphylla* Linn:

Commonly known as 'devil-pepper' and vernacular names are Borachadar, nagmani.

Several, steroids, triterpenoids, steroidal glycosides, flavonoids, saponins, catechin, phenolics and alkaloids have been reported which show potent antioxidant activity[56].Plants produce a great number of secondary metabolites like alkaloids, terpenes and polyphenolic compounds, many of which, are known to possess therapeutic applications [57]. *Rauvolfia tetraphylla has* highest flavonoid content among the five species of this genus [55].

XXV.*Tabernaemontana divaricata*(L.)R.Br. ex Roem.&Schult:

Also called crape jasmine or pinwheel flower, which exudes milky latex and its local name 'tagar'. In various assays particularly DPPH, the plant showed antioxidant activity. Several known and yet unknown oxidants are supposedly present in this plant [58]. Flavonoids and some other phytochemicals are found in higher concentrations[59]. The major classes of alkaloids are present within the genus, like monoterpene indole, bisindole alkaloids. Other compounds include terpenes, lactones, steroids, phenolics and flavonoids each of which related to antioxidant property[60].

XXVI.*Telosma pallida* (Roxb.) W. G. Craib:

This plant is called Telosma vine. Antioxidant capacity of methanolic extract of leaves and stem was found highest as IC50 values were 253.12±1.02, 158.43±0.48 respectively [61]. Antioxidant power may be due to the presence of phenolics, flavonoids and some other chemicals like alkaloids, glycosides, saponins, sterols and tannin [61].

XXVII.*Thevetia peruviana*:

Common name yellow oleander, local name 'kolke' with enormous milky latex. Various flavonoids and phenolic compounds were detected in the collected latex, namely nirigin, rutin, quercetin, kaempferol, luteolin, hesperdin, catechin[62]. Methanolic extract contained highest amounts of phenolic compounds and exhibited the maximum antioxidant activity. The *in vitro* DPPH assay showed high scavenging property of methanolic extract 69.79±0.12, and this may be due to hydroxyl groups existing in the phenolic compounds-[20].

XXVIII.*Tylophora fasciculate* Buch.-Ham. ex Wight:

Vernacular name is 'ishermul'. In phytochemical studies the presence of alkaloids, flavonoids, phenols, saponins, steroids, tannins and terpenoids was confirmed by qualitative analysis and potent antibacterial activity of the plant extracts [63] was established. The active constituent phenanthroindolizidine alkaloid, tylophorine and huge content of phenolics have been [64]. The % DPPH scavenging activity increases with the increasing concentration. The concentration of the plant extract of *Tylophora indica* needed for 50% inhibition (IC50) was found to be 199.58µg/ml, whereas 194.58 µg/ml needed for ascorbic acid [64].

XXIX.*Vallaris solanaceae*(Roth) Kuntze:

The plant is woody climber and local name is 'ramsar'. The seed of this planthas several compounds like glycosides of vallaroside, solanoside, vallarosolanoside, 16-diacetyl-16-anhydro-acoschimperoside P, mono-O-acetyl-

acoschimperoside P, mono-O-acetyl-vallaroside and mono-O-acetyl- solanoside[65]. Leaf extract showed various compounds, such as carbohydrates, flavonoids, saponins, phenols, tannins, glycosides, steroids [66]. In DPPH assay, ethanolic extract showed 53.75% inhibition [67].

Phenols, carotene, xanthophyll, sterols, different alkaloids, glycosides, saponins etc. are exclusively important bioactive components with diverse biological functions including antioxidant capacity. Due to presence of their OH groups, act as non-enzymatic radical scavengers with tremendous effect.

Table 1: Comparison of antioxidant capacity based on DPPH assay among 29 species.

Sl. NO.	Accepted botanical names	Synonyms (TPL, 2013)	Activity
1.	*Allamanda blanchetii* A.DC	*Allamanda violacea* Gardner	**M**
2.	*Allamanda cathartica* L.	*Allamanda cathartica* var. *grandiflora* L.H.Bailey& Raffill	**L**
3.	*Allamanda schottii* Pohl	*Allamanda schottii* Hook.	**YNR**
4.	*Alstonia scholaris* (L.) R.Br.	*Echites scholaris* L.	**H**
5.	*Calotropis gigantea* (L.)Dryand.	*Calotropis gigantea* (L.) R. Br. ex Schult.,	**H**
6.	*Calotropis procera*(Aiton) W.T. Aiton	*Calotropis heterophylla* Wall.ex Wight	**H**
7.	*Carissa carandas* L.	*Carissa carandas* var. *congesta* (Wight) Bedd.	**L**
8.	*Carissa spinarum*L.	*Carissa abyssinica*R. Br.	**M**
9.	*Catharanthus roseus* (L.) G.Don	*Catharanthus roseus* var. *roseus*	**H**
10.	*Catharanthus pusillus*(Murray) G. Don	*Lochnera pusilla* (Murray) K.Schum.,	**YNR**
11.	*Cryptolepis dubia* (Burm.f.)M.R.Almeida.	*Cryptolepis buchananii* Roem. &Schult.	**YNR**
12.	*Gymnema sylvestre*(Retz.) R. Br. ex Schult	*Gymnema sylvestre* var. *affine* (Decne.) Tsiang,	**H**
13.	*Hemidesmus indicus* (L.) R. Br. ex Schult.	*Periploca indica* L.	**L**
14.	*Holarrhena pubescens* Wall.exG.Don	*Holarrhena antidysenterica* (L.) Wall.exA.,	**H**
15.	*Holostemma annularis* K.Schum	*Holostemma ada-kodien* Schult.	**M**
16.	*Ichnocarpus frutescens* (L.) W.T. Aiton	*Apocynum frutescens* L.	**H**
17.	*Nerium indicum* Mill.	*Nerium indicum* subsp. *kotschyi* (Boiss.) Rech.f.	**H**
18.	*Nerium oleander* L.	*Nerium oleander* subsp. *kurdicum* Rech.f.	**H**
19.	*Pergularia daemia*(Forsk.) Chiov.	*Pergularia daemia* var. *daemia*,	**L**
20.	*Plumeria acutifolia Poir*	*Plumeria acutifolia* var. *gasparrinii* A.DC.	**H**
21.	*Plumeria obtusa* L.	*Plumeria obtusa* var. *laevis* Griseb.	**L**
22.	*Plumeria rubra* L.	*Plumeria rubra* f. *acuminata* (W.T.Aiton) Woodson,s	**M**
23.	*Rauvolfia serpentina* (L.) Benth. ex Kurz	*Rauvolfiaobversa*(Miq.)Baill	**H**
s24.	*Rauvolfia tetraphylla* L.	*Rauvolfia hirsuta* Jacq.	**YNR**
25.	*Tabernaemontana divaricata*(L.)R.Br. ex Roem.&Schult	*Tabernaemontana coronaria* (Jacq.)Willd.,*Vinca alba* Noronha	**M**
26.	T*elosma pallida* (Roxb.) W. G. Craib	*Pergularia pallida* (Roxb.) Wight &Arn.	**H**
27.	*Thevetia peruviana*	*Thevetia peruviana* f. *aurantiaca* H.St.John	**H**
28.	*Tylophora fasciculata* Buch.-Ham. ex Wight	*Tylophora indica*	**M**
29.	*Vallaris solanaceae*(Roth) Kuntze	*Vallaris anceps (Dunn &R.S.Williams) Wall. Ex C.E.C.Fisch*	**M**

Abbreviations like H,M,L and YNR indicate the magnitude of inhibition

H= High (more than 60% inhibition), M= Moderate (more than 40% inhibition), L= Low (less than 40%), YNR= Yet Not Reported

4. Conclusion

Due to oxidative stress, always our body is facing several outrageous diseases like cancer, ulcer, liver injury, cardiovascular disease etc. The above result showed that plant extract of most of the species of Apocynaceae family are important agents with tremendous effect for removal of oxidative radicals i.e., ROS, which are responsible for imposing oxidative stress in our body. Among these 29 selected species *Catharanthus sp, Rauvolfia sp, Gymnema sylvestre, Holarhhena pubescens, Alstonia scholaris, Nerium sp and Calotropis sp* are strong enough as potential source for natural antioxidants.

The results and information revealed that the Apocynaceae plant species are potent and generating highly effective source of ROS scavengers to combat oxidative stress related deadly diseases. Majority of the ethnic and tribal peoples from Purulia district, West Bengal completely depend on the plant-based medicine for their regular healthcare. So, this comprehensive review ascertains the standard of plant-based herbal formulation of drugs which could be of great value for management of human healthcare, particularly for resource poor tribal communities of Purulia district.

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Research Article

Evaluation of phenol content, antibacterial and antioxidant potential of six polypore fungi

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Abstract

This study focuses on antioxidant activities (DPPH free radical scavenging), total phenolic content and antibacterial activities of selected six Polypore fungi belonging to the family Polyporaceae, collected from different regions of forest areas in the Purulia district, West Bengal, India. The phenol content of the samples ranges from 1.8404 ± 0.125747 µg/ml to 11.2608 ± 0.947625 µg/ml. Folin-Ciocalteu reagent is used to measure the phenolic content and its Gallic acid equivalents have been calculated. Higher free radical scavenging activity is observed in lower IC50 (50% inhibition concentration) values. IC50 values range from 49.84 µg/ml to 3993.62 µg/ml. Our results reveal that fungi having higher concentration phenolic content have positive effects against pathogenic bacteria. It shows better antibacterial and antioxidant activities.

Key Words: Antioxidant, Antibacterial, Phenol content, Macrofungi, Polyporaceae

1. Introduction

Macro fungi are essential for antibacterial compounds to survive in their natural environment. Antimicrobial compounds can be extracted from plants [1] and many basidiomycetes species and some of them have potential effects on humans [2]. Many antibiotics that are usually used in the clinical pathway, are extracted from fungi and actinomycetes. During the last few years, several pathogenic microorganisms developed resistance against the available antibiotics. Infections caused by *Candida* sp., *Staphylococcus epidermidis*, *Staphylococcus aureus*, *Streptococcus* sp., *Enterococcus* sp. and *Escherichia coli* create multidrug-resistant (MDR). Consequently, we are looking for new antibiotics with novel mechanisms due to emerging drug-resistant pathogenic variants [3-5]. Antimicrobial activities of basidiomycetes fungus from different countries were emphasized. As part of a screening programme designed to assess the antimicrobial activity of basidiomycetes, 317 isolates representing 204 species were collected in Spain and subjected to testing against a variety of human clinical pathogens [6]. In a study, 103 isolates of basidiomycetes fungi belonging to 84 species were found in various locations of Brazil among which 14% of macrofungal extracts were effective against one or more microorganisms [7]. Seventy-five per cent of tested polypore fungi exhibit potent antimicrobial activity, and these could be a valuable resource to produce new antibiotics. Numerous substances derived from these fungi generate antiviral, cytotoxic, and anticancer compounds [8]. The phenolic compounds have antibacterial activity against diverse pathogenic bacteria [9]. Secondary metabolites are beneficial to health and many of them attributes antioxidant, antimicrobial, anticancer, cholesterol-lowering and immunostimulatory properties [10-12]. Phenolics shows strong antioxidant activity [13]. It works as an effective radical scavenger and offers protection from UV radiation or pathogen aggression [14].

In this study, six wild polypore fungi viz *Pycnoporus sanguineus*, *Microporus xanthopus*, *Cubamyces flavidus*, *Lentinus polychrous*, *Cerrena hydnoides* and *Coriolopsis occidentalis*, from Purulia district, have been examined for their phenolic content, antibacterial capabilities, and DPPH activities. We report that relatively higher phenolic contents show better antibacterial activity and some wild polypore fungi involve better free radical compounds.

2. Materials and Methods

Test sample and organism: We have studied the antimicrobial activity, total phenolic content, and DPPH assay from six isolates of basidiomycetes fungus (Plate: 1) belonging to the family Polyporaceae. Antibacterial activity of *Pycnoporus sanguineus* (L.) Murrill, *Microporus xanthopus* (Fr.) Kuntze, *Cubamyces flavidus* (Lév.) Lücking, *Lentinus polychrous* Lév., *Cerrena hydnoides* (Sw.) Zmitr., *Coriolopsis occidentalis* (Klotzsch) Murrill; were tested against one gram-positive pathogenic microorganism *Enterococcus faecalis* (MCC 3037) and seven gram-negative pathogenic bacteria *E. coli* (MCC 3099), *Pseudomonas aeruginosa* (MCC 4242), *Eneterobacter cloacae* (MCC 3111), *Proteus mirabilis* (MCC 3895), *Salmonella enterica* (MCC 4378), *Chromobacterium violaceum* (MCC 2216), and *Escherichia fergusonii* (MCC 4329).

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Extraction procedure for antimicrobial test: Six polypore fungi have been collected from different areas of the forest region in Purulia District, West Bengal. The samples are dried at 35°C in a hot air oven for seven days. Completely dried samples are powdered using a grinder separately. One gram of each powder sample was mixed with 12 ml of each of the solvents-methanol, Dimethyl sulfoxide (DMSO), and cocktail [15-16] (dH2O: ethyl alcohol: methyl alcohol: acetone: chloroform in 1:2.5:2.5:2:2 ratio) in separate airtight conical flasks for 48 hours at 50°C in a rotary incubator shaker for homogenization. Each sample was rubbed separately in a mortar pestle and the solvent extracts were kept separately. Extracts were centrifuged at 8000 rpm for 20 minutes and supernatants were collected separately.

Agar well diffusion method: Antimicrobial activities of test fungi were carried out by well diffusion technique following [17]. Fresh bacterial cultures (100 µl) were pipetted and placed at the centre of sterile petriplates containing media (Luria-Bertani with Kanamycin media was used for *Salmonella enterica* and *Chromobacterium violaceum* and nutrient agar for rest 6 bacterial strains) and spread over petriplates using the spread plate technique. After spreading the fresh bacterial culture, seven wells were prepared (one for control and six for test samples) with the help of a sterilized cork borer. Fungal extracts (250 µl) were added to each well and Petri plates were incubated for 24 hours at 37°C temperature.

Gallic acid standard solution preparation: Standardization of gallic acid was measured according to Hayet *et al.* [18]. Here 0.100 mg of gallic acid dissolves in 10 ml of 80% methanol and then the volume is made up to 100 ml with distilled water in a 100 ml volumetric flask. This gallic acid stock solution was diluted with distilled water to create calibration standard solutions of 20, 40, 60, 80, and 100 µg/ml. One ml of 10% FCR, 10 ml of 7% Na2CO3 (Sodium carbonate), and 4 ml of distilled water were added to each solution. The precursor solutions were allowed to settle for 1 h in dark at room temperature. Finally, the absorbance of these solutions was measured in a UV-vis spectrometer (Shimadzu UV-1800) at 750 nm and the graphical presentation is shown in Fig1.

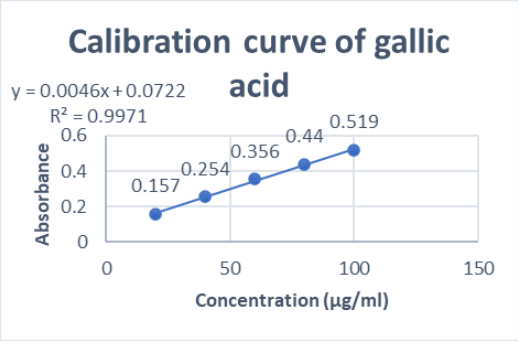

Fig. 1: Linearity curve of gallic acid solution

Estimation of the total phenolic content of the samples: 1 gm of each of the powdered samples of polypore fungi was mixed with 10 ml of methanol in separate airtight conical flasks. Conical flasks were kept in the water bath for two days at 45°C. Then each mixture was ground in a mortar pestle, and centrifuged at 4000 rpm for 20 minutes. The supernatants were collected separately and 100 µl of each of the extract solutions was added with one ml of ten times diluted FCR. After five minutes, 10 ml 7% Na2CO3 was added to each of the test tubes. Each experiment was repeated in triplicate. Finally, the absorbance is measured at 765 nm with the help of Uv-vis spectrophotometer.

Extraction procedure for DPPH assay: 500 mg of each of the powdered samples was mixed with 10 ml of methanol in an airtight container and kept the mixture in a hot air oven at 45°C for 48 hours. The ground samples were centrifuged at 4000 rpm for 20 minutes. 1 ml of each of the supernatants was considered in separate test tubes and diluted up to 10 ml with the same solvent (Methanol).

2,2-Diphenyl-1-picrylhydrazyl assay method: Free radical scavenging activities of methanolic extracts were measured using DPPH (2,2-Diphenyl-1-picrylhydrazyl) assay [19]. We have taken various concentrations (50, 100, 150, 200, and 250 µg/ml) of the methanolic extracts of samples. 0.75 µl stock solutions of DPPH (1.3 mg/ml in methanol) were added to each test tube. Test tubes were shaken well and kept in a dark condition for 30 minutes at room temperature. The absorbance was measured at 517 nm using Uv-vis spectrophotometer. 98% methanol was used as blank and the percentage of DPPH free radical scavenging was measured by the following equation [20-22].

% Inhibition = {(Z Control – Z Sample) / Z Control} x 100

Z Control - Absorbance of the control sample, (Methanol + DPPH)

Z Sample - Absorbance of Sample in different concentrations, (Sample + DPPH)

IC50 (50% inhibition concentration) values were calculated from the % inhibition.

3. Results

Antibacterial activity: A total of six polypore fungi have been selected to observe their antimicrobial activity against one gram-positive [*Enterococcus faecalis*, (MCC 3037)] and seven gram-negative bacteria [E. coli, (MCC 3099),

Pseudomonas aeruginosa (MCC 4242), *Eneterobacter cloacae* (MCC 3111), *Proteus mirabilis* (MCC 3895), *Salmonella enterica* (MCC

4378), *Chromobacterium violaceum* (MCC 2216), *Escherichia fergusonii* (MCC 4329)]. We observed that the DMSO extract of fungi *Pycnoporus sanguineus* shows sensitivity against bacterial strain *Enterococcus faecalis* (MCC 3037), and *Escherichia fergusonii* (MCC 4329), Cocktail extraction of fungus *Pycnoporus sanguineus* shows inhibitory effect against bacterial strain *Chromobacterium violaceum* (MCC 2216). DMSO extract of *Microporous xanthopus* shows inhibitory results against bacterial strain *Eneterobacter cloacae* (MCC 3111), and cocktail extract of *Microporous xanthopus* shows sensitive results against bacterial strain *Escherichia fergusonii* (MCC 4329). DMSO extract of, *Cubamyces flavidus* has a potential impact against bacterial strain *Chromobacterium violaceum* (MCC 2216). Cocktail extract of *Lentinus polychrous* shows inhibition against bacterial strain *Enterococcus faecalis* (MCC 3037) (Table 1). DMSO extract of *Pycnosporus senguineus* shows the zone of inhibition (25.644 ± 0.381222) against pathogenic bacteria *Enterococcus faecalis* (MCC 3037) and the zone of inhibition (20.098 ± 0.503954) against *Escherichia fergusonii* (MCC 4329). The cocktail extract of *P. senguineus* was effective (10.636 ± 0.396396) against the bacterial strain *Chromobacterium violaceum* (MCC 2216)

Test fungi	**Solvents**	**Bacterial strains**							
		MCC 4242	MCC 3111	MCC 3037	MCC 3895	MCC 4378	MCC 2216	MCC 4329	MCC 3099
Pycnoporus sanguineus	METHANOL	-	-	-	-	-	-	-	-
	DMSO	-	-	+	-	-	-	+	-
	COCKTAIL	-	-	-	-	-	+	-	-
Microporus xanthopus	METHANOL	-	-	-	-	-	-	-	-
	DMSO	-	+	-	-	-	-	-	-
	COCKTAIL	-	-	-	-	-	-	+	-
Cubamyces flavidus	METHANOL	-	-	-	-	-	-	-	-
	DMSO	-	-	-	-	-	+	-	-
	COCKTAIL	-	-	-	-	-	-	-	-
Lentinus polychrous	METHANOL	-	-	-	-	-	-	-	-
	DMSO	-	-	-	-	-	-	-	-
	COCKTAIL	-	-	+	-	-	-	-	-
Cerrena hydnoides	METHANOL	-	-	-	-	-	-	-	-
	DMSO	-	-	-	-	-	-	-	-
	COCKTAIL	-	-	-	-	-	-	-	-
Coriolopsis occidentalis	METHANOL	-	-	-	-	-	-	-	-
	DMSO	-	-	-	-	-	-	-	-
	COCKTAIL	-	-	-	-	-	-	-	-

Table 1: The antimicrobial activities of six macrofungal extracts against eight pathogenic bacteria. The '+' sign indicates a positive result (with a zone of inhibition) & '-' sign indicates a negative result (without a zone of inhibition)

DMSO extract of *Microporus xenthopus* is effective (12.38 ± 0.424382) against the bacteria strain *Eneterobacter cloacae* (MCC 3111) and cocktail extract shows effectiveness (19.15 ± 0.221811) against microbial strain *Escherichia fergusonii* (MCC 4329). DMSO extract of, *Cubamyces flavidus* inhibits the growth (13.458 ± 1.021112) of bacterial strain *Chromobacterium violaceum* (MCC 2216) and cocktail extract of *Lentinus polychrous* also inhibits the growth (12.658 ± 0.261859) of bacterial strain *Enterococcus faecalis* (MCC 3037) (Table 2).

Name of fungi	**Concentration of extraction (1g/12ml)**	**Bacterial strain**	**Zone of inhibition (mm)**
Pycnoporus sanguineus	DMSO	MCC 3037	25.644 ± 0.381222
		MCC 4329	20.098 ± 0.503954
	COCKTAIL	MCC 2216	10.636 ± 0.396396
Microporus xanthopus	DMSO	MCC 3111	12.38 ± 0.424382
	COCKTAIL	MCC 4329	19.15 ± 0.221811
Cubamyces flavidus	DMSO	MCC 2216	13.458 ± 1.021112
Lentinus polychrous	COCKTAIL	MCC 3037	12.658 ± 0.261859

Table 2: The zone of inhibition with standard deviation value of Pathogenic bacteria against 7 positive test samples

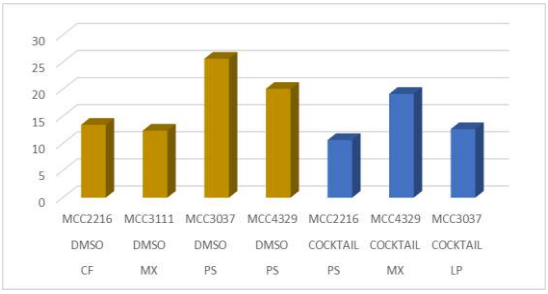

Fig 2: Graphical representation of bacterial strain with their zone of inhibition (in mm) in different solvent (PS: *Pycnoporus sanguineus*, MX: *Microporus xanthopus*, CF: *Cubamyces flavidus*, LP: *Lentinus polychrous*)

Total phenolic content: The phenolic content (Table 3) of the test sample was as follows: *Lentinus polychrous* (11.2608 ± 0.947625)> *Pycnoporus sanguineus* (10.75357 ± 0.502006)> *Cubamyces flavidus* (7.927467 ± 1.972585)> *Microporus xanthopus* (6.5506 ± 0.763484)> *Coriolopsis occidentalis* (3.362233 ± 0.204967)> *Cerrena hydnoides* (1.8404 ± 0.125747). *Lentinus polychrous* and *Pycnoporus sanguineus* had shown the highest phenolic content while lowest phenolic content was observed in *Cerrena hydnoides*. It was observed that the higher percentage of phenol content of the samples is more effective against bacterial strain than the lower percentage of phenolic.

Name of sample	**Sample absorbance**	**Phenol concentration (µg/ml)**
Pycnoporus sanguineus	0.123	10.75357 ± 0.502006
	0.123	

	0.119	
Microporous xanthopus	0.099	6.5506 ± 0.763484
	0.106	
	0.102	
Cubamyces flavidus	0.110	7.927467 ± 1.972585
	0.117	
	0.099	
Lentinus polychrous	0.122	11.2608 ± 0.947625
	0.129	
	0.121	
Cerrena hydnoides	0.081	1.8404 ± 0.125747
	0.081	
	0.080	
Coriolopsis occidentalis	0.089	3.362233 ± 0.204967
	0.087	
	0.087	

Table 3: Quantitative analysis of the total phenolic content of six macrofungal samples

DPPH free radical scavenging activity: DPPH (2,2- diphenyl-1-picrylhydrazyl) method was used in this study to assess the antioxidant activity of methanolic extract of six different polypore fungi. The result demonstrated that we have considered different concentrations (50 µg/ml, 100 µg/ml, 150 µg/ml, 200 µg/ml, 250 µg/ml) of methanolic extract from the samples. In most cases, the IC50 value (50% inhibition concentration) is used to demonstrate DPPH scavenging activity. The IC50 value of the test sample was as follows *Cubamyces flavidus* (49.84 µg/ml) > *Coriolopsis occidentalis* (451.38 µg/ml) > *Lentinus polychrous* (697.34 µg/ml) > *Microporus xanthopus* (2220.22 µg/ml) > *Pycnoporus sanguineus* (3483.84 µg/ml) > *Cerrena hydnoides* (3993.62 µg/ml). In this study, *Cubamyces flavidus* performed the highest antioxidant property. So, 49.84 µg/ml *Cubamyces flavidus* show 50% free radical scavenging activity and *Cerrena hydnoides* show the lowest free radical scavenging activity (Table 4)

Concentration (µg/ml) of fungal extracts	**Inhibition%**	**DPPH IC50, (µg/ml)**
Pycnoporus sanguineus		
50	0.88±0.26	3483.84
100	1.65±0.31	
150	2.30±0.21	
200	3.01±0.10	
250	3.77±0.09	
Microporus xanthopus		
50	1.24±0.13	
100	1.48±0.23	

150	1.63±0.05	2220.22
200	4.80±0.12	
250	5.07±0.03	
Cubamyces flavidus		
50	4.5±0.50	49.84
100	9.3±0.30	
150	13.56±0.04	
200	17.9±0.35	
250	23.8±0.12	
Lentinus polychrous		
50	3.28±0.40	697.34
100	7.69±0.35	
150	12.4±0.34	
200	14.5±0.5	
250	17.06±0.21	
Cerrena hydnoides		
50	1.03±0.20	3993.62
100	1.74±0.03	
150	2.45±0.06	
200	2.97±0.02	
250	3.52±0.06	
Coriolopsis occidentalis		
50	6.30±0.51	451.38
100	10.76±0.25	
150	18.03±.78	
200	22.04±0.42	
250	28.01±.78	

Table 4: DPPH radical scavenging of the extract from fungi at the different concentration level

Plate 1: Photographs of Polypore Macrofungi: a. *Pycnoporus sanguineus;* b. *Microporus xanthopus;* c. *Lentinus polychrous;* d. *Cerrena hydnoides;* e. *Coriolopsis occidentalis;* f. *Cubamyces flavidus*

4. Discussion

The result of present study shows that Methanolic extraction of this test fungi showed no significant antibacterial activities against pathogenic bacteria. DMSO and cocktail were found to be the best solvents for the solubilization of bioactive components for polypore fungi. The fungi with Phenol content ranges from 6.5506 µg/ml to 11.2608 µg/ml had shown better antibacterial activities. Relatively higher phenolic content of *Pycnoporus sanguineus* and *Lentinus polychrous* may be responsible for antibacterial activity against the gram-positive bacterial strain *Enterococcus faecalis* (MCC 3037). Similarly high phenol content of *Cubamyces flavidus* and *Microporous xanthopus* may be corelated with their antibacterial properties against three gram-negative bacterial strains (Table 2 and Table 3). *Cubamyces flavidus* has shown (49.84µg/ml) the best antioxidant activities, whereas, *Cerrena hydnoides* has shown the least (3993.62 µg/ml) activity. Further details metabolite profiling of the test fungi may open a new horizon for discovering drugs against pathogenic bacteria.

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Review Article

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A Comprehensive review on Use and Abuse of Nitrogen in Agriculture

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Abstract

Nitrogen, a vital element for plant growth, is pivotal in modern agricultural practices. Its responsible application enhances crop yields, ensuring food security for a growing global population. Nitrogen-based fertilizers have revolutionized agriculture by supplying plants with the nutrients necessary for robust growth and increased productivity. However, the widespread use of nitrogen fertilizers has led to unintended consequences, such as water pollution, greenhouse gas emissions, and soil degradation. While proper nitrogen fertilization boost crop yields and addresses nutrient deficiencies, excessive application can result in the release of reactive nitrogen compounds into the environment. These compounds can contaminate water bodies through runoff, leading to harmful algal blooms, oxygen depletion, and aquatic ecosystem disruption. Additionally, nitrogen fertilizers contribute to nitrous oxide emissions, a potent greenhouse gas that exacerbates climate change. Mitigating the negative impacts of nitrogen abuse in agriculture requires a multifaceted approach. Precision agriculture techniques, such as targeted fertilization based on soil nutrient levels, can minimize excessive nitrogen application. Cover cropping, crop rotation, and agro forestry practices improve soil health, reducing the need for synthetic fertilizers. Enhanced nitrogen recovery systems and the adoption of organic farming methods also hold promise in curbing nitrogen-related issues. Nitrogen's indispensible role in modern agriculture is undeniable, but its misuse poses significant environmental challenges. Striking a balance between harnessing nitrogen's benefits and mitigating its detrimental effects is essential for sustainable agricultural practices and safeguarding the planet's ecosystems. Adapting innovative farming strategies and fostering awareness about responsible nitrogen use will be crucial in addressing the complexities surrounding this vital element in agriculture.

Key Words: Nitrogen, Fertilizers, Pollution, Policies, Economic Instruments

1. Introduction

The fundamental elements upon which life is dependent are nitrogen, nitrogen oxides, carbon atoms, hydrogen atoms, oxygen atoms, and phosphorus atoms. [1]. Among them, N is the fundamental element in the formation of amino acids, which, in turn, are the basic components of proteins. Nitrogen (N) makes up 78 % of the air, where it is virtually inert and largely non-reactive, existing mainly in molecular (N2) form. Nitrogen gas cannot be absorbed by living matter in the atmosphere. Human protein consumption depends on the ability of plants to incorporate N into their food chain and it requires certain transformations to be used by plants and later by animals for this to happen.

Fertilizing with nitrogen (N) has proven to be one of the most effective methods of increasing crop yield over the past 60 years. Nitrogen induced increase in yield may be related to increased production of panicles in cereals and pods in legumes. Nitrogen also decreases the sterility of grain and increases the weight of grain [2, 3]. The NO3 – movement in soil profile is six times higher than NH4+ with flowing water and is therefore prone to leaching loss. [4] On the other end, Ammonium (NH4 +) and NO3 are major plant available forms of N in soil. Owing to its positive charge, NH4 + has very poor mobility in negative charged soils of the subtropical climate [5].

The use of any form of fertilization, whether it is inorganic or organic, can have a detrimental effect on the environment if not properly managed. In the past, large quantities of nitrogenous (N) fertilizers were utilized worldwide. However, the rate of recovery or effectiveness of nitrogenous fertilizers in the cultivation of crops on arable land is low, with an estimated recovery rate of 25-50% of the fertilized N [6]. The increasing utilization and expense of nitrogen fertilizers in agricultural production is cause for concern. By increasing N use efficiency, yields and profits can be increased by an average of $18.75 per acre when cultivating grain crops with minimal environmental impact [7].

In agriculture, nitrogen (N) is added to fields to increase crop yields. However, nitrogen is also a critical nutrient for plants to grow and develop, but it is also a limiting nutrient for aquatic ecosystems. As a result, nitrification of excess nitrous oxide (N and/or phosphorus, P) from consuming contaminated groundwater has been associated with a number of downstream consequences, such as accelerated surface water erosion, blooms of

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algae and hypoxia and public health problems. Nitrogen loss to the environment occurs when it leaches to the groundwater and is transported to the surrounding surface waters by surface run off, or directly to the surface waters by tile drainage by bypassing stream buffers [8, 9].

In this review, I discuss various factors controlling N use efficiency and the methods which can improve N use efficiency in agriculture minimizing environmental losses. This review is the first of its kind to look at all the research that's been done on how to use both inorganic and organic sources of N to make it better. N use efficiency in different crops in a single work. We specify possible ways to improve N use efficiency for future research.

Nitrogen sources and how they interact with plants and soil

Nitrogen is a naturally occurring element that can be found almost everywhere. It's mostly nitrogen gas (N2) in the atmosphere, making up about 78% of the total amount of nitrogen gas (4000 trillion tons). Dinitrogen is broken down into different forms like ammonium and nitrite by bacteria and other organisms [10]. About 95% nitrogen is naturally occurring organic matter in the soil. [10]. However, when looking at nitrogen from an agricultural perspective, it is clear that certain sources of nitrogen are responsible for the majority of nitrogen available to plants and crops. These nitrogen sources can be either natural or organic, and can also be generated through artificial processes. Natural nitrogen is found in soils through the mineralization of minerals and the fixation of bacteria [11]. In soil, nitrogen is available in the form of ammonium or nitrate [12]. In soil, nitrogen is also present in the form of nitrites, nitrous oxides, and atmospheric nitrogen. However, these forms of nitrogen are not naturally available to plants unless they are transformed into ammonium or nitrates through bacterial or lightning fixation [12]. Another source of nitrogen is stored in living cells. When cells die, they decompose and release nitrogen back into the soil. Legumes and animal carcasses typically contain more nitrogen than other living things, making them excellent natural nitrogen fertilizers [13, 14]. The use of leguminous crops in crop rotations is a method of fixing atmospheric nitrogen and subsequently depositing it into the upper levels of agricultural soils. The high nitrogen content of animal bone or bone meal is utilized as an effective substitute for chemical fertilizers [15, 16]. Nitrogen is sourced primarily from the atmosphere, where it constitutes about 78% of the air. It's often obtained through a process called nitrogen fixation, where certain bacteria convert atmospheric nitrogen into forms that plants can absorb. Additionally, nitrogen is found in organic matter, like decaying plants and animal waste.

In terms of interactions, nitrogen is crucial for various biological processes. It's key component of amino acids, which are building blocks of proteins. Plants use nitrogen to grow and develop and its availability can impact crop yield. However, excessive nitrogen in soil and water can lead to environmental issues like water pollution and eutrophication. Balancing nitrogen levels is essential for sustainable agriculture and ecosystem health.

Nitrogen in the Environment

Nitrogen is a crucial element in the environment, existing in various forms like nitrate, nitrite, and ammonia. It's essential for plant growth and is often a component of fertilizers. However, excess nitrogen from agriculture and industrial processes can lead to environmental issues like water pollution, algal blooms, and soil degradation. The acquisition and disposal of nitrogen in the agri-ecological system is linked to a variety of intricate and interconnected processes. The primary causes of nitrogen loss in agricultural systems include: (a) gaseous emissions in the form of volatilization or denitrification of ammonia; (b) leaching (i.e., removal of nitrogen below the root zone by percolating water); (c) plant uptake; and (d) surface run-off. To understand the nitrogen cycle, a simple mathematical equation can be used.

$$N\ net = N\ [e + bf + c + om + min.] - N\ [pl + g + i + l + r\ ]$$

The positive sign shows that N has been added to the soil and the negative sign shows that the soil has been depleted of N. N net is the net amount of N added to the soil. e is electrical discharge, bf is biological fixation, c is chemical fertilizer, om is organic manure, min is mineralization, pl is plant uptake, g is emissions (volatilization , denitrification) i is immobilization, l is Leaching and r is surface runoff. The losses associated with plant uptake and surface runoff are relatively low. However, the losses due to volatilization are significant at a pH level typically higher than 8.0, in soils with a high temperature and low cation exchange capacity. Anoxic soil conditions are conducive to denitrification. The leaching of NO_3^- into groundwater is more hazardous to human health than other chemical elements [17].

Problems Associated with excessive Nitrogen in the Environment

Nitrogen fuels and facilitates good growth of plants. However, plant species have different

nitrogen-response values because of their inherent growth rate dichotomy and their response to other related changes such as acidification or nutrient imbalances. As a result, it seems that every farmer needs to be seriously trained in the art of fertilizer application. Most importantly, the rate of fertilizer that plants need relative to their normal functioning must be determined, without causing damage to the environment.

The traditional method of fixing nitrogen biologically is beneficial to the environment; however, it is not sufficient to meet the current growing demand for food. As a result, the addition of nitrogen fertilizer to agricultural ecosystems in order to improve the yield of crops has been adopted, which has seen a dramatic rise in the past 50 years [18]. The long-term consequences of over-application of N often lead to surface water being eutrophicated, a phenomenon commonly referred to as highly toxic to water bodies. Drainage canals have long been a means of transporting nitrate and phosphate effluents out of paddy fields and into rivers or lakes. This is most commonly observed when paddling releases pond water. Percolation tends to purify soil layers, but leaching works its way out of the soil and acts as a powerful deterrent to the system.

Rain and irrigation are two of the best ways to spread fertilizer further into the soil than it can reach from the root zone. Over time, this can lead to groundwater contamination. Rain and irrigation are great harbingers of contamination because they cause nitrate fertilizers to react on the soil surface, which in turn causes nitrogen to be lost to the atmosphere [19, 20] also concedes the fact that natural processes, such as intensive watering and large amounts of rainfall, also remove excess surface nitrogen fertilizer, contaminating waterways. Hypoxia, which is a low level of dissolved oxygen in comparison to algal blooms, is caused by high nitrate levels in waterways, which can be toxic to warm blooded animals at 10 mg/L or higher if left unchecked [21, 22]. Excessive nitrogen in the environment can lead to various problems, such as water pollution, air pollution, and ecosystem disruptions. It can cause nutrient imbalances, harmful algal blooms, and contribute to greenhouse gas emissions. Additionally, excessive nitrogen can negatively impact human health, aquatic life, and biodiversity.

Atmosphere Pollution

Nitrogen pollution from agriculture primarily stems from the excessive use of synthetic fertilizers and poor management of livestock waste. When these sources release nitrogen compounds into the atmosphere, they can contribute to the formation of airborne pollutants like ammonia (NH_3) and nitrous oxide (N_2O). Ammonia can affect air quality, and nitrous oxide is a potent greenhouse gas that contributes to climate change. There are direct health effects of air pollution. In 2017, 5 million people died due to air pollution-related diseases. The United States and China have the highest mortality rates among the top 10 countries [23]. Agricultural activities account for nearly 15% of global greenhouse gas emissions each year [24, 25]. Human activity is responsible for between 60% and 80% of global (N_2O) emissions. [26,27]. N_2O is a greenhouse gas that remains 298 times more powerful than carbon dioxide in the atmosphere due to the growing use of N fertilizer in food production around the world [28].

However, some recent research on corn cropping systems shows an exponential correlation between them [29, 30]. According to the latest estimates made by the Intergovernmental Panel on Climate Change (IPCC), the current global average N_2O emitted by nitrogen fertilizers is just under 0.9 % of the N used in the cropland [31]. This means that, every 100 kg of nitrogen fertilizer used in agriculture releases 1.0 kg nitrogen dioxide (N_2O) into the atmosphere [29]. Agricultural nitrous oxide (N_2O) emissions to the atmosphere reached 7.718 Gg in 2018 [32]. Sustainable practices such as precision farming, proper fertilizer application, and efficient manure management are crucial. These measures can help minimize nitrogen emissions, reduce environmental impact, and promote healthier air quality.

Aquatic Ecosystems Pollution

Aquatic ecosystems can be adversely impacted by pollution from agricultural nitrogen. Excessive use of nitrogen-based fertilizers can lead to runoff off nitrogen compounds into nearby water bodies, causing problems such as nutrient enrichment, algal blooms, oxygen depletion, and harm to aquatic life. This phenomenon, known as eutrophication, disrupts the balance of the ecosystem and can have cascading effects throughout the food chain. It's important for agricultural practices to be managed sustainably to mitigate these pollution effects and protect aquatic ecosystems. Nitrate concentrations are a fundamental factor in assessing the level of contamination in aquatic systems, as they are the most consistent form of N and their high concentration disturbs the essential equilibrium of aquatic organisms [33, 34].

Agriculture is one of the main contributors to nitrate leaching [35–38]. Nitrogen leaching depends not only on the amount of fertilizer used, but also on other factors such as the time and location of fertilizer application in relation to the growing cycle of the crop, irrigation techniques, fertilizer types, agronomic techniques, crop rotations, soil properties, soil cover, climatic

conditions, etc. [39–45]. A sustainable population is incompatible with the depletion of groundwater aquifers. Groundwater is being used more and more to meet increasing water demands. Today, 43% of all irrigation water and 50% of all domestic water consumption worldwide are sourced from groundwater [46]. Contamination of this resource is therefore a serious threat to the health of those who rely on it. Numerous studies have shown that long-term use of water with a nitrate content above 50 (mg/L) increases the risk of some types of cancer [47–49]. In the 1990s, the first research was conducted on the production of toxins by cyanobacteria in polluted aquatic environments [50, 51]. Cyanobacteria colonize the surface of the body of water where the highest concentration of solar radiation occurs, causing the water to turn green and blocking light from reaching the deeper layers of the water [52]. When vegetation and many floating algae reach the new limit of photosynthesis, they die due to a reduction in nutrients, which are then broken down by bacteria that, during their activity, absorb oxygen and create toxins. As a result, native aquatic species die due to a lack of oxygen and are replaced by species more suitable for anaerobic conditions. At a deeper level, the cold temperatures and lack of oxygen and light create an unviable habitat for vernacular living organisms [53]. Eutrophication affects many inland and coastal bodies of water around the world [54] and life in some of the world's oceans is threatened. Carpenter and Bennett [55] mention that the maximum acceptable nutrient intake limit for wetland, lakes and freshwater has already been reached.

Sustainable Nitrogen management policies

It's been shown that all of these strategies and methods are effective at increasing crop yields and reducing diffuse N pollution from the agriculture industry. But farmers don't seem to be very happy with the Best management Practices (BMPs) and they have a few obstacles to overcome when it comes to changing their farming methods [56, 57]. It is essential to comprehend how farmers make decisions in order to enhance fertilizer management [58].

It typically includes policies aimed at reducing nitrogen pollution, improving agricultural practices and improving ecosystem health. Examples include regulating industrial nitrogen emissions, increasing fertilizer use, promoting crop rotation and promoting wastewater treatment solutions. These policies need to be tailored to each region's unique needs and challenges. Public policies to reduce N pollution will only be effective if they match the incentives that drive farmers to switch management modes. The focus should be on reinforcing positive messages that emphasize the advantages of these BMPs [59].

Policies

Environmental policies, in general aims, are all about internalizing, stopping, and fixing the outside effects of economic activity. Regarding N use as fertilizer, we've already talked about the externalities in the previous posts, and these policies are all about changing farmers' management practices. Different countries have different levels of environmental regulations, and each has different farmer requirements.

Some specific policy approaches that can contribute to the sustainable management of nitrogen. Fertilizer management, introduce guidelines for responsible fertilizer use, including precision agriculture techniques, proper timing, and dosage to minimize excess nitrogen application. Nutrient trading programs, establish programs that allow farmers to trade nutrient credits, incentivizing those who adopt practices that reduce nitrogen runoff or emissions. Cover crops and crop rotation encourage the use of cover crop rotation to improve soil health, reduce nitrogen leaching, and increase nutrient efficiency. Regenerative agriculture it support practices like agroforestry, agroecology, and organic farming that emphasize holistic approaches to reduce nitrogen runoff and enhance soil health. Wastewater treatment upgrades, sewage treatment plants to effectively remove nitrogen from wastewater before it's released into water bodies.

Kanter et al. [58] propose the concept of a complete food chain NUE as a new framework for analyzing policies to reduce N pollution. In their study, the authors argue that, due to the close interdependence between all the players in the food supply chain, reducing N losses at the farm level can only be achieved by implementing non-farmer-oriented policies. In the US, there are a few rules about how to use fertilizer, like how to plan it and what it should contain. But there's not much federal regulation about how to use it. Most of the time, it's just a bunch of free programs. And the amount of nitrogen oxide in the air is up for grabs [60]. Currently, there is very little regulation on N pollution in China. However, due to the high levels of pollution in air and water in many Chinese regions, the China Ministry of Agriculture initiated an ecological-based reform of the subsidy system [61]. The effectiveness of these policies varies depending on local circumstances, socio-economic considerations, and stakeholder engagement. Combining these strategies in a context-specific way can lead to a more sustainable approach to nitrogen management.

A social intervention related to nitrogen use could focus on raising awareness and encouraging responsible nitrogen management practices among farmers and the broader agricultural community. To educate farmers about the importance of responsible nitrogen use and promote practices that reduces nitrogen pollution while maintaining agricultural productivity. To organize workshops and training sessions for farmers to inform them about the impacts of nitrogen pollution, best practices for nitrogen application, and techniques to improve nutrient efficiency. Information dissemination, to develop educational materials such as pamphlets, videos, and infographics, explaining the effects of nitrogen runoff on water quality and ecosystem health. Distribute these materials at agricultural fairs, markets, and community centers. Peer-to-peer learning, facilitate peer learning networks where experienced farmers who have successfully adopted sustainable nitrogen practices can share their knowledge and experiences with their peers. Create mobile apps or websites that provide farmers with easy access to information about nitrogen management, including calculators for optimal fertilizer application based on soil type and crop. Collaborate with agricultural organizations and government agencies to provide incentives for farmers who adopt sustainable nitrogen practices. These incentives could include subsidies for financial support for equipment, or recognition for best practices. It would be difficult to compile a comprehensive list of current and potential policies around the world that could be implemented to enhance agricultural N management, as each nation has its own regulations with varying levels of rigidity. For instance, in the United States, agricultural policies are based on voluntary initiatives, as exemplified by the Environmental Quality Initiatives Program. As for China, the world's largest user of nitrogen fertilizers, there is a growing awareness of the need for improved environmental protection, which is reflected in high-level regulations such as the recently reintroduced National Environmental Protection Act, which provides for severe penalties for companies that do not adhere to environmental regulations [62].

Economic Instruments

As far as taxes are concerned, economists have suggested that the cost of fertilizer would need to double in order to produce fertilizer savings [63], the review of the European Union's fertilizer taxation system reveals that, on the whole, the efficiency of pricing remains limited [64]. Provide financial incentives, subsidies, or tax breaks to farmers adopting nitrogen-reducing practices. Alternative tools for improving pollution control under the EUN Directive have recently been studied by several authors, such as [65], manure application standards would be a more effective way to limit nutrient surplus to soils than a nutrient surplus tax, according to researchers alternatives for reducing N on dairy farms.

Technical Innovations

The use of precision irrigation and drip irrigation is also on the rise and has been supported by many governments [66]. Utilizing energy conservation technologies also makes fertilization (the use of fertilizer through irrigation water) easier. Chen et al. [61] show that innovation subsidies are an effective way to reduce agricultural emissions. While production subsidies are harmful to the environment (for example, in China) innovation subsidies reduce total emissions of pollutants while increasing the farmer's bottom line.

CONCLUSION

Nitrogen’s dual nature as a crucial agricultural asset and an environmental liability underscores the need for conscientious management practices. While nitrogen-based fertilizers have revolutionized food production, their unchecked use can lead to severe ecological consequences. Striking a balance between maximizing agricultural output and minimizing the negative impacts of nitrogen requires a collaborative effort involving farmers, policymakers, researchers, and consumers. By adopting precision techniques, embracing sustainable farming methods, and advocating for responsible nitrogen use, the agricultural sector can ensure its viability while safeguarding the environment for current and future generations.

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Review Article

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Urban biodiversity: a double-edged sword

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Abstract

Urban biodiversity is a complex but promising phenomenon that allows humans and wildlife to coexist in cities. Green urban spaces serve as vital habitats, connecting natural areas and fostering biodiversity. Despite challenges such as habitat loss, it Has been observed that bird population are adapting and few plant species taking refugees in road side and railway track. Designing environmentally friendly green spaces is critical for balancing urban development with the natural environment. Infrastructure projects have an indirect impact on green spaces, necessitating sustainability-focused strategies. Soil improvement and sustainable water management, according to research, promote native plant growth. Urban biodiversity management necessitates a harmonious blend of conservation and economic development, fostering investment in environmentally friendly green spaces that mitigate the negative effects of urbanization while preserving biodiversity.

Keywords: Urban biodiversity, Green urban spaces, Habitat loss, Environmentally friendly green spaces, Sustainable management

1. Introduction

Urbanization, an unstoppable force in our modern world, is rapidly transforming the Earth's landscapes, converting once-pristine natural habitats into sprawling cities and suburbs. This relentless expansion poses significant threats to the delicate tapestry of life that we call biodiversity. Yet, within the confines of concrete and steel, urban environments also present unique opportunities for the coexistence of humans and wildlife. In this essay, we embark on a journey through the double-edged nature of urban biodiversity, where we venture into the heart of bustling metropolises to explore both the potential benefits and inherent challenges it brings.

Urban areas, marked by their bustling streets, towering skyscrapers, and constant human activity, may not appear as sanctuaries for biodiversity at first glance. However, hidden beneath the concrete jungle lies an intricate web of life, awaiting our understanding and appreciation. Indeed, cities have the potential to serve as vital refuges for certain species, contributing to the conservation of biodiversity in unexpected ways. The presence of green spaces, such as parks, gardens, and street trees, provides essential habitats and resources for a surprising variety of plant and animal species [1]. These urban green oases act as essential stepping stones, connecting fragmented natural habitats and facilitating the flow of genes among populations [2]. Furthermore, urban areas, with their proximity to human activities, support a diverse range of species that display a remarkable tolerance for our presence, often resulting in the remarkable phenomenon of high species richness within city limits [3].

The presence of thriving urban bird populations is a shining example of the positive aspect of urban biodiversity. Birds have proven to be remarkably adaptable to urban life's challenges, capitalizing on the resources provided by green spaces and anthropogenic food sources [4]. Surprisingly, urban habitat provides them with protection from predators that exist in natural ecosystems, contributing to higher breeding success rates for some bird species [5]. Furthermore, studies have shown that urban areas can provide vital stopover sites for migratory birds on their long journeys [6]. Cities are thus more than just concrete jungles; they are home to a diverse avian community, which contributes to the overall conservation and genetic diversity of bird species.

Nevertheless, amidst the skyscrapers and bustling streets, urbanization brings with it a plethora of challenges for biodiversity. The relentless march of development results in the destruction and fragmentation of natural habitats, leading to the loss of native species and a decline in the vital ecosystem services they provide [7]. Even more

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concerning is the introduction of exotic species, which often occurs as an unintended consequence of urbanization. These newcomers can outcompete and displace native species, pushing them to the brink of extinction and ultimately causing a decline in overall biodiversity [8]. Additionally, the pollutants that accompany urban life, such as air and water pollution, further hinder the movement and survival of wildlife in urban areas [9]. Artificial barriers like roads and buildings create physical obstacles, isolating populations and disrupting essential migratory routes.

The alarming decline of native bee populations, critical pollinators that support ecosystem functioning and global food security, is a stark example of the negative impact of urban biodiversity. Urbanization has a direct impact on their foraging opportunities by reducing the diversity of floral resources and exposing them to harmful pesticides [10]. The extinction of native bees not only impedes plant reproduction but also disrupts the intricate ecological networks of which they are a part [11].

Urban biodiversity emerges as a complex and multifaceted phenomenon in the intricate movement between human progress and the natural world. As we traverse the dynamic landscape of urban environments, it becomes increasingly apparent that the future of biodiversity, both within and beyond city limits, is intrinsically linked to our ability to understand, appreciate, and mitigate the dual nature of urbanization's impact on the ecosystems we share with countless species.

Table 1: Two school of thoughts: Positive and negative aspects.

Two school of thoughts	**Positive Aspects**	**Challenging Aspects**
High richness of plants and animals	Cities can host a high richness of plants and animals [12].	Urbanization destroys and fragments natural ecosystems [13].
Efficient use of land	Compact living allows for the efficient use of land, enabling cities to preserve valuable green spaces and protect biodiversity [14].	Urbanization poses challenges to ecological sustainability [15].
Novel biotic communities and habitats	Urbanization creates novel biotic communities and habitats **[13].**	The spatial arrangements of habitats, species pools, and a species' adaptability and natural history affect the actual occurrence of a species **[13].**
Vibrant and diverse urban culture	Cities can support a vibrant and diverse urban culture, fostering creativity, innovation, and social interaction [16].	The role of non-native species in urban landscapes is complex **[13].**
Social thinking dimension	Urbanization can become a positive force, helping cities thrive despite an uncertain future [17].	Urbanization can cause harm to the environment. [15]
Natural aspect or further urbanization	Urbanization can create chances to support the natural aspects of city green spaces [12].	Protected areas can have both positive and negative effects because they can encourage urban development in their vicinity [18].

2. Positive Aspect:

2.1. Ecological Benefits:

- Increased species diversity: Urban areas with high biodiversity can support a variety of plant and animal species, leading to healthier and more resilient ecosystems.

- Improved ecosystem services: Biodiversity in urban settings can enhance pollination, nutrient cycling, soil fertility, and water regulation, thus improving overall environmental quality.

Gaston et al., 2010 [19] discuss how having more green and diverse natural areas in cities can improve general well-being, help the economy, and protect the environment. Blanco and their team, 2021 [20], discuss a new approach to city planning. They want to make cities work more like natural ecosystems and help the environment. They think this can make people and nature healthier. But, we still need to study more to make sure these ideas work better. We need to understand how ecosystems work and how they help us. Newman et al., 2011 [21] mentioned that “Biophilic Urbanism" means designing cities with nature in mind, like having plants and green spaces in and around buildings. Many important government goals, such as combating climate change, making cities cooler, using less energy, and making people healthier and happier, can benefit from this. Aznarez et al. 2023 [22] found that socioeconomic and historical factors, particularly luxury (wealth-related) and legacy (historical management), influence urban nature distribution and characteristics in Vitoria-Gasteiz, Basque Country. Higher education levels were associated with higher urban biodiversity (luxury effect), whereas older areas had more plant cover and ecosystem services (legacy effect), but this was associated with lower biodiversity due to recent biodiversity-promoting efforts. The luxury effect was amplified by habitat quality, and the legacy effect was amplified by population density, highlighting the interplay of these factors in shaping urban ecosystems. Marselle and colleagues2021 [23] argue that caring for nature in cities is a smart way to improve public health. They claim that biodiversity, or the presence of a diverse range of plants and animals, is essential for maintaining the health of our environment, which in turn helps to maintain the health of people. This way of thinking places urban biodiversity at the heart of both nature conservation and making cities healthier for residents. It shows how nature in cities can be good for both the environment and the well-being of the people who call those cities home.

According to Soanes et al., 2023 [24], urban biodiversity conservation is critical to addressing the global biodiversity crisis and fostering a connection between people and nature. It highlights that urban biodiversity is often overlooked in urban planning and management. Protected areas, green infrastructure, and citizen science projects are examples of current conservation practices. However, challenges to urban biodiversity conservation include a lack of funding, a lack of political support, and a lack of awareness of its importance. Collaboration between government, non-governmental organizations, and communities, as well as the use of innovative technologies and citizen science initiatives, are all enabling factors. This review emphasizes the importance of a multidisciplinary approach and calls for greater awareness and understanding of the importance of urban biodiversity among decision-makers and the general public.

According to Faeth et al., 2012 [25], as cities grow, the environment becomes fragmented and transformed, affecting the types of plants and animals that can live in these areas. Mao et al., 2013 [26] emphasizes that urbanization results in a shift in the distribution of biodiversity, leading to a decrease in native flora and fauna and an increase in non-native species, resulting in greater uniformity. Faeth et al., 2012 [25] also mentioned that while urban areas may have a greater variety of plants due to the introduction of non-native species, there is typically a reduction in the diversity of animals such as herbivore and pollinators, chances of crop failure. Shwartz et al., 2013 [27] underscores the significance of local-scale management in maintaining biodiversity in small green spaces within cities. In summary, urban biodiversity tends to exhibit reduced native biodiversity and increased non-native biodiversity, with the overall impact on species diversity varying depending on the specific group of plants and animals and the particular urban context. Now it's a good time to look at the natural places in cities because we can learn about things like how communities are affected, how areas change, and how new species come in and live with the ones already there.

Milliken, 2018 [28] reported on the economic benefits of urban ecosystem services, emphasizing the importance of presenting these benefits in monetary terms for the understanding of policy and decision makers. Various tools, such as the green infrastructure valuation toolkit and i-Tree software, were highlighted as valuable for quantifying the economic value of ecosystem services, including pollution removal, carbon storage, storm water reduction, and more. These economic valuations offer a comprehensive framework to assess the returns on investment in urban landscape schemes. Furthermore, it was noted that urban morphology plays a pivotal role in the provision of multiple ecosystem services, and the development of dense, compact cities can impact service provision and urban biodiversity. Engineered green infrastructure, like green roofs

and vertical greening systems, provides opportunities to enhance connectivity in densely populated areas, creating ecological networks that facilitate the flow of benefits dependent on these structures. Urban planning should harness these tools to foster a synergy between ecosystem services and human well-being.

Ecosystem services are vital benefits provided by nature, spanning provisioning, regulating, cultural, and supporting services. Urban areas, including green infrastructure, are hubs for generating these services. Provisioning encompasses urban farming and resource recycling. Regulating services mitigate pollution and offer carbon storage, noise reduction, and temperature control. Cultural services enhance mental health and community well-being, making their recognition essential in urban planning. Supporting services, rooted in habitat provision and biodiversity, are fundamental to all ecosystem services. Expressing these services in economic terms aids decision-making. Urban planning's focus on connectivity and engineered green infrastructure is key to maximizing these urban benefits.

2.2 Aesthetics and Well-being:

Psychological benefits: Urban areas with diverse flora and fauna can provide a sense of connection to nature, promoting mental well-being, stress reduction, and improved quality of life.

Visual appeal: Green spaces and wildlife habitats within cities enhance the aesthetic quality of urban environments, making them more attractive places to live and visit.

Urbanization has become an increasingly prominent facet of modern society, transforming the landscape and altering the environment in profound ways [29]. As our cities expand and human populations surge, urbanization carries with it a set of environmental challenges that are both intricate and far-reaching. One of the key components in understanding and addressing these challenges lies in unraveling the intricate relationship between urban development and the natural world. This is where urban-rural gradient studies enter the scene, offering a valuable lens through which to examine the impact of urbanization on biodiversity [30]. There is immediate need to study the intriguing patterns that emerge as one traverse the spectrum from densely populated urban epicenters to the less altered, more pristine rural landscapes. This scrutinizes how plant and animal populations change along this continuum, revealing a host of transformations that provide crucial insights into the intersection of human civilization and the natural world. As transformations are the physical changes that escalate as approaching the urban core, with surges in population density, is mirrored by a surge in road density, more polluted air and soil, notable shifts in temperature and precipitation patterns, and the proliferation of impervious surfaces, such as pavement and buildings. Concurrently, urban areas are characterized by an increased import of resources intended for human use, further exacerbating their impact on the environment. The process of construction in urban areas, so intrinsic to urbanization, often brings with it the grim tale of habitat destruction. Trees fall, vegetation vanishes, and topsoil is displaced. This upheaval translates into a significant loss of native biodiversity. Even after construction is completed, the urban environment continues to be unforgiving, as paved surfaces consume vast tracts of potential habitat, leaving little room for native species. What remains is often graced with nonnative vegetation, further undermining the preservation of local biodiversity. The urban environment, with its unique set of challenges and opportunities, also plays host to an increasing proportion of nonnative species as one venture deeper into the urban core. The swelling human population densities in this region facilitate the importation of these nonnative species, giving rise to a vibrant but often disruptive array of inhabitants.

The journey to preserve and restore biodiversity in this urban landscape is marked by a twofold approach - preservation and restoration. Urbanization casts a complex shadow upon the inhabitants of the natural world, and the degree of adaptation to urban life varies across species. This differentiation gives rise to three distinct categories: "urban avoiders," "urban adapters," and "urban exploiters," each demonstrating varying degrees of dependence on human resources, from minimal reliance to complete dependency [31].

3. Negative Aspect:

3.1 Habitat Destruction:

The construction of buildings, roads, and other urban infrastructure can result in the direct destruction of natural habitats, such as wetlands, forests, and grasslands. In this context Land conservation can buffer local climate changes and enhance genetic diversity, but human intrusions must be managed. Potential solutions include treating ecosystem services as an urban utility, protecting biodiversity hotspots under urbanization pressure, and international coordination for urban sustainability. Urban areas

significantly impact ecosystem services, especially freshwater provision, which is crucial for residential, industrial, and commercial purposes. However, urban areas also affect the quality and quantity of available freshwater resources, posing challenges for many cities, particularly those in semiarid and arid climates [32]. Urbanization also impacts regulatory hydrological services, leading to increased surface water runoff and the vulnerability of downstream communities to flooding due to impermeable surface area expansion. Urban areas depend on upstream natural habitats for regulating water flows, creating a complex interdependence [33]. To minimize habitat and biodiversity loss and protect ecosystem services, cities should integrate ecological knowledge into urban planning practices [34]. Effective urbanization strategies require the coordination of ecological knowledge and practices between researchers and stakeholders, including citizens, community organizations, planners, and government representatives [35]. Research on urbanization's impact on biodiversity and ecosystem services raises questions about urban-rural interactions, feedback mechanisms, and cultural values [36]. Interdisciplinary approaches are vital to understanding trade-offs in ecosystem services for various urban socio-economic groups. The development of a theoretical framework, including cultural services, is crucial for inclusive urban planning [37].

3.2. Climate Change:

Urban areas often have a higher concentration of greenhouse gas emissions, contributing to climate change, which can affect the distribution and behavior of many species. In context of climate change microbes, plants, and animals, serve as crucial indicators of climate change impacts on ecosystems, aiding in the mobilization of public support and political action [38]. The first and foremost observation it has been observed the changes in plant trait like canopy height, leaf area, and specific leaf area [39]. These changes challenge assumptions of nutrient limitation in the face of climate warming (due to Elevated atmospheric CO2) or physiological mal functioning [40]. Another study shows that climate change and its consequences are likely to affect micronutrient malnutrition by limiting the availability of micronutrient-rich plant and animal foods rather than their micronutrient content (41). Here the need of the hour to identify the key stone species - Keystone species are essential not only for conserving biodiversity but also for safeguarding ecosystem services and promoting resilience against environmental challenges [42]. Recognizing their multidimensionality should guide conservation efforts, emphasizing their role in maintaining ecological communities and processes [43]. According to Timóteo et al., 2021 [44] global meta-analysis emphasized that keystone species' importance extends across multiple niche dimensions, impacting various ecosystem functions. Removing or reducing keystone species can trigger ecological disruptions, affecting the stability and functionality of ecosystems. Recognizing the multifaceted role of keystone species is crucial for biodiversity conservation and ecosystem resilience. Conservation management should consider the complexity of interactions in natural systems, as the removal of a single keystone species can have far-reaching consequences. Conservation of keystone species can indirectly safeguard entire ecosystems and the species dependent on them, contributing to both biodiversity conservation and ecosystem resilience [43]. This keystone species thrive only when they capable to live on multiple niches-and in case of animals - Maternal effects played a significant role in shaping these differences, challenging the assumption of a direct link between habitat preferences and reproductive success.

While these negative aspects of urban biodiversity are significant, it's also essential to acknowledge the positive aspects. Urban areas can provide refuge for some species, and there are opportunities for conservation efforts, urban greening, and sustainable urban planning that can enhance biodiversity and support coexistence between humans and nature.

Urbanization, through its habitat destruction and creation, can favor both native and non-native species adapted to urban environments, potentially leading to a loss of biodiversity in natural ecosystems and the introduction of non-native species [13]. Human presence in urban areas triggers avoidance behavior in wildlife, underscoring the role of human disturbance in wildlife population declines [45]. However, the presence of wild plants and animals in neighborhoods may not align with resident preferences [46]. Despite these negative impacts, urban areas can host diverse plant and animal species, supporting various ecosystem services [47], and contribute to achieving the Convention on Biological Diversity's goal of biodiversity preservation [13]. Through strategic planning and a commitment to sustainable practices, cities can navigate the challenges of urbanization, working towards a more environmentally friendly, inclusive, and prosperous future.

Addressing these challenges typically entails implementing strategies like urban planning, conservation efforts, and involving communities to foster eco-friendly, diverse urban spaces, while the "double-edged sword" concept underscores the

importance of balancing urban development with biodiversity conservation in cities.

3.3 Pollution:

Urban areas can be significant sources of pollution, including air pollution, water pollution, and noise pollution. These pollutants can harm wildlife and disrupt ecosystems, leading to declining biodiversity. Pollution can also lead to a loss of biodiversity in natural ecosystems and the introduction of non-native species. Human-caused disturbance, resource changes, and loss of environmental heterogeneity in urban ecosystems are known to affect soil biodiversity, and cause the differences observed between urban and natural soil systems [48].

3.4. Invasive Species:

- Introduction of non-native species: Increased urban biodiversity may include invasive species that can disrupt native ecosystems, outcompeting local species and causing ecosystem imbalances. Non-native species can prey upon or compete with native species, leading to declines in their populations and potentially causing local extinctions.

The example of the negative impact of non-native species is the kudzu vine (Pueraria montana), which is an invasive plant species in the southeastern United States that can grow rapidly and smother native vegetation [49]. Another example is the European starling bird (Sturnus vulgaris), which is a non-native bird species in North America that can outcompete native bird species for nesting sites and food (www.nwf.org) [50]. Polygonum cuspidatum is an invasive plant species in the UK that can cause damage to buildings and infrastructure [51]. Heracleum mantegazzianum- giant hogweed this is an invasive plant species in North America that can cause severe skin irritation and blindness [49]. Bromus tectorum, known as downy brome, drooping brome or cheatgrass, is a winter annual grass native to Europe, southwestern Asia, and northern Africa; it greens up and sets seed earlier than most native species, giving it an advantage over slower-growing native species (www.fs.usda.gov) [52]. It can prevent native plant germination by depleting soil moisture in the spring. Lantana camara, water hyacinth, and Parthenium are harmful in India for different reasons. They harm the environment and local plants, sometimes causing allergies in people and animals.

Leucaena leucocephala, another invasive plant, is a problem in various places due to its fast growth and how it harms local plant diversity. It may also affect other plants by stopping them from growing properly.

A study by Mello & Oliveira in 2016 [53] looked at how Leucaena affects native plants on a Brazilian island. In the lab, it didn't seem to stop the native Erythrina velutina from growing. But in the wild, Erythrina had a harder time near Leucaena trees. The local Capparis flexuosa plant sometimes helped Erythrina and sometimes didn't. When both Capparis and Leucaena were around, they hurt Erythrina more than Leucaena alone; showing that different plants can affect each other in complicated ways when one is invasive.

3.5 Human-Wildlife Conflicts:

- Property damage and health risks: A higher diversity of wildlife in urban areas can result in conflicts such as crop damage, property destruction, and increased risks of zoonotic diseases.

- Safety concerns: Urban ecosystems with high biodiversity may attract potentially dangerous species, such as venomous snakes or aggressive animals, posing risks to human safety.

In a study Narango et al., 2018 [54] showed the negative impact of nonnative plants on insectivorous birds and the ecosystems they inhabit. These nonnative plants disrupt the natural balance by reducing the availability of insects, which are a vital food source for insectivorous birds. This disruption has far-reaching consequences for the entire ecosystem.

For example, the study conducted on Carolina chickadees in residential areas shows that as nonnative plants increase, the bird population's ability to find enough insects and reproduce declines. It's also noteworthy that maintaining nonnative plants at less than 30% of the plant biomass is necessary to sustain bird populations. This research highlights the importance of prioritizing native plant species in efforts to restore human-dominated areas, as these plants are crucial for supporting the local food web and maintaining a healthy ecosystem.

Johnson and their team [55] looked at how invasive plants can thrive or struggle in new environments when they interact with other species. They focused on three invasive plants, Japanese knotweed and its close relatives, which are known troublemakers in North America and Europe. These invasive plants have a trick up their sleeves – special nectar-producing parts that attract friendly insects in their home in Japan. But

when they were taken to North America as decorative plants, they also brought along some foes, like the Japanese beetle, which became a common pest. The scientists wanted to figure out how these insect interactions affected the success of these invasive plants in North American cities. They checked out things like ants visiting the plants, how many Japanese beetles were around, their eating habits, and other stuff like who came to the flowers and how seeds were made.

What they found was quite interesting. Most of the plant damage in North America was done by Japanese beetles, but it was not as bad as in Japan. This means these invasive plants had fewer enemies in their new home. And here's a cool tidbit: ants liked the new leaves of these plants more than the older ones, and Japanese beetles usually munched on the older leaves. Also, native ants in North America visited the nectar parts of these invasive plants, and some even protected them from Japanese beetles. To top it off, both native and non-native insects visited the plants' flowers, helping make seeds. So, the study suggests that native and non-native species, through their actions like pollinating and protecting, can help these invasive plants spread. This is a big deal and reminds us of the importance of keeping native plant species in cities to help local insects and keep our environments healthy.

According to a study by Sun et al., 2023 [56], suggests that the absence of plant biodiversity in urban areas can lead to an increase in termite aggression, ultimately resulting in substantial damage to wooden property. The study found that human-caused disturbance, resource changes, and loss of environmental heterogeneity in urban ecosystems can affect soil biodiversity and cause differences observed between urban and natural soil systems. The loss of top predators and altered habitat characteristics in urban ecosystems can result in functionally destabilized food-webs, including those in soil, and result in changes to trophic cascades that benefit certain soil biota groups, including termites. The study suggests that promoting plant biodiversity in urban areas can help reduce termite aggression and damage to wooden property.

The dynamics of urban ecosystems, specifically in relation to insects and disease vectors, reveal complex interactions influenced by a variety of factors. The loss of top predators, such as birds of prey, and alterations in habitat characteristics within urban environments can lead to destabilized food webs, affecting trophic cascades. This, in turn, can benefit certain soil biota groups, including termites, ants, and snails. These organisms pose risks as they can potentially damage buildings, hinder plant performance, and transmit human pathogens. Such perturbations in urban settings highlight the delicate balance of ecosystems in the face of urbanization.

In the context of mosquito vectors and urbanization, studies have indicated a concerning trend. Urbanization processes contribute to the proliferation of mosquito vectors of anthroponotic vector-borne diseases, exemplified by Aedes aegypti and Culex quinquefasciatus in Miami-Dade County, Florida. A natural enemy is another mosquito Toxorhynchites splendens entirely non-blood feeding feed on the larvae of pest species and other aquatic insects and consume larvae of other mosquito species occurring in tree crevices [57].

Furthermore, urbanization is linked to changes in mosquito biodiversity, and this has implications for mosquito-borne viruses. Decreased mosquito biodiversity is associated with higher levels of urbanization, fostering conditions where arboviruses thrive, often tied to the prevalence of a single predominant mosquito species like Culex perexiguus. This connection underscores the need to understand the intricate relationship between urban growth and the emergence of arboviruses.

3.6. Urbanization Pressures:

While urban biodiversity provides numerous ecological and aesthetic benefits, it is crucial to address the negative aspects and implement measures for sustainable urban planning and management. Balancing the advantages with the potential pitfalls can lead to a healthier coexistence between urban environments and their inhabitants.

Urbanization, characterized by the rapid expansion of cities and human settlements, is one of the most significant drivers of habitat loss and fragmentation, as well as the intensification of the urban heat island effect. This essay explores the impact of urbanization pressure on the loss and fragmentation of habitats, as well as the formation of urban heat islands [18].

3.7. Habitat Loss and Fragmentation

The process of urbanization involves the conversion of natural landscapes and ecosystems into urban areas, resulting in the loss of critical habitats for various plant and animal species. Encroachment upon natural habitats leads to habitat destruction, as entire ecosystems are cleared for the construction of buildings, infrastructure, and roads [58]. This loss of natural habitats directly impacts biodiversity and disrupts ecological processes.

Moreover, urbanization causes habitat fragmentation, where remaining natural areas become isolated patches surrounded by an urban matrix. Fragmentation of habitats can have severe

consequences for wildlife by reducing connectivity and disrupting migration patterns, leading to decreased genetic diversity, increased isolation, and higher extinction rates [59]. The decline of species richness and the disruption of ecological interactions are common outcomes due to habitat loss and fragmentation.

3.8. The Urban Heat Island Effect

The urban heat island effect refers to the phenomenon where cities experience significantly higher temperatures compared to surrounding rural areas. Urbanization intensifies the heat island effect by altering land use patterns, modifying vegetation cover, and increasing the amount of impervious surfaces, such as concrete and asphalt [60]. These changes result in reduced evapotranspiration, increased heat absorption, and limited natural cooling mechanisms.

The rise in temperatures in urban areas can have detrimental consequences on human health, energy consumption, and overall ecological processes. Excessive heat exposure can lead to heat exhaustion, heatstroke, and even increased mortality rates, particularly among vulnerable populations [61]. The urban heat island effect also exacerbates the demand for energy, as air conditioning and cooling systems are required to maintain comfortable indoor temperatures. Additionally, elevated temperatures in urban areas can disrupt natural processes, such as altering plant growth patterns, affecting wildlife behavior, and reducing water availability.

The pressure of urbanization leads to habitat loss, fragmentation, and the exacerbation of the urban heat island effect. These impacts have severe consequences for biodiversity, ecological functioning, and human well-being. It is crucial to recognize the importance of preserving and restoring natural habitats within urban areas and implementing sustainable urban planning strategies that prioritize green spaces, promote connectivity, and mitigate the urban heat island effect. By doing so, we can create more livable cities that coexist harmoniously with nature, protect biodiversity, and enhance the overall quality of life for urban residents.

4. Strategies for Sustainable Urban Planning

4.1 Designing Ecologically Friendly Green Spaces

The significance of ecologically friendly green spaces in urban development cannot be overstated. Urban planning in places like Surabaya should prioritize ecological balance as a fundamental goal. This means that the design and development of urban areas must aim to maintain a harmonious relationship between human progress and the natural environment. The challenges faced in highly populated metropolitan regions, such as Rungkut Madya Street, underscore the need for this balance. These areas often contribute significantly to pollution and environmental issues, including dust, heat, and noise pollution, adversely affecting the quality of life for residents.

Infrastructure projects of two roads in Rungkut Madya Street, Java, Indonesia, could encourage the conversion of green areas into buildings due to the high value of land along these roads, leading to a decrease in overall greenery. To tackle these issues and enhance the urban environment, a qualitative research technique was used to observe and characterize existing green spaces with the primary aim of improving streetscapes and green space design [62].

Urban green spaces, including parks, gardens, and urban forests offer numerous environmental, social, and health benefits, such as improved air quality, reduced urban heat island effects, and recreational opportunities. However, as cities expand and urbanization progresses, the design and management of green spaces must evolve to address environmental concerns. This study explores strategies for developing environmentally friendly green spaces, emphasizing the incorporation of sustainable approaches and the preservation of biodiversity.

The significance of ecologically friendly green spaces is twofold. Firstly, well-designed green spaces can mitigate the urban heat island effect by providing shade and cooling through evapotranspiration, thereby reducing energy consumption for cooling buildings. Secondly, these spaces contribute to biodiversity protection, which is crucial for the sustainability of local ecosystems. Maintaining a diverse range of plant and animal species in urban green spaces is essential, as highlighted by Dallimer et al., 2019 [63]. Ecologically friendly green areas can attract and support animal populations by cultivating a varied range of natural flora and providing habitat niches, thereby contributing to urban biodiversity conservation. In Latvian urban green space planning, two primary factors take precedence: aesthetics and ecology [64].

In Eugene, Oregon, the Friendly Area Neighborhood employed Delphi analysis to explore various planting plans aimed at enhancing urban ecosystem services. Stakeholder priorities, identified through surveys and Delphi analyses,

include air quality, storm water quality, native plantings, and pollinator habitats. The willingness of residents to provide financial support influenced the development of diverse planting options. Reshaping urban green spaces, as emphasized by Devy et al., 2009 [65], necessitates the involvement of multiple stakeholders, including local municipality architects and, significantly, community residents. Furthermore, it must adhere to the principle of adaptive co-management.

Ecologically friendly green space design principles emphasize the selection of native plants. In Edmonton, Alberta, Canada, research by Rojas et al., 2021 [66] demonstrated that soil amendment with compost and proper site preparation positively influences the naturalization of native trees and shrubs in urban environments, leading to improvements in soil texture, acidity, electrical conductivity, and total carbon.

A study conducted by Calviño et al., 2023 [67] emphasizes the critical role of green roofs in urban green infrastructure. Green roofs offer environmental benefits, including providing habitats for arthropods. With the rising adoption of green roof technology in South American cities, the selection of local or alien plant species becomes crucial for their success. The study employs an integrative multicriteria decision framework to assess the potential of native and alien plant species on green roofs. The research, conducted in Córdoba, Argentina, compares the performance of six native and six foreign species on 30 experimental green roofs. The findings reveal that native plants, even without management, outperform alien species, displaying higher occurrence and somewhat greater cover. Notably, native annuals demonstrate the ability to reseed the following season, underscoring the importance of longevity as a relevant plant feature for future research.

Green spaces can also be instrumental in sustainable water management. Rain gardens and permeable pavements, as exemplified in the study by Song, 2022 [68], are sustainable water management strategies that help minimize runoff and improve water quality while educating people about the importance of water conservation. Such elements can contribute to the overall sustainability of green spaces, creating environmentally friendly urban environments that enhance the quality of life for residents.

In conclusion, the design and development of ecologically friendly green spaces are essential components of urban planning. These spaces not only mitigate the negative impacts of urbanization, such as the urban heat island effect and habitat loss, but also contribute to the preservation of biodiversity and the overall well-being of urban residents. Incorporating native plants, involving the community, and adopting sustainable water management practices are crucial steps in achieving the ecological balance necessary for harmonious urban development.

5. Conclusion

Urban biodiversity is indeed a double-edged sword, as it presents both opportunities and challenges. While urban areas can support a diverse range of species and contribute to conservation efforts, the process of urbanization also leads to habitat loss, fragmentation, and the introduction of invasive species, which negatively impact native biodiversity. However, it is crucial to recognize that urban biodiversity can be managed in a way that is sustainable for both the ecology and the economy.

Finding a balance between ecological conservation and economic development is imperative for creating truly sustainable cities. Sustainable urban planning can integrate green spaces, such as parks, gardens, and tree-lined streets, which not only provide habitats for wildlife but also enhance the quality of life for urban residents. Implementing measures to protect and restore natural habitats within cities, while also promoting connectivity and biodiversity corridors, can mitigate the negative effects of urbanization on biodiversity.

Furthermore, considering the economic benefits derived from urban biodiversity can encourage policymakers and urban planners to prioritize its preservation. Urban ecosystems offer numerous ecosystem services, including improved air and water quality, temperature regulation, and pollination, which directly contribute to human well-being and economic prosperity. Recognizing the economic value of urban biodiversity can help encourage investments in conservation and sustainable urban development.

The design and development of ecologically friendly green spaces are essential components of urban planning. These spaces not only mitigate the negative impacts of urbanization, such as the urban heat island effect and habitat loss, but also contribute to the preservation of biodiversity and the overall well-being of urban residents. Incorporating native plants, involving the community, and adopting sustainable water management practices are crucial steps in achieving the ecological balance necessary for harmonious urban development

In conclusion, urban biodiversity presents both challenges and opportunities. By acknowledging the double-edged nature of urban biodiversity and promoting sustainable practices that prioritize both ecological conservation and economic development, we can create cities where humans

and wildlife can coexist harmoniously. Striking this balance will ensure that urban areas not only thrive economically but also maintain healthy and vibrant ecosystems, ultimately leading to a more sustainable future for all.

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On the Distribution of Poles of Meromorphic Functions in the Light of Slowly Changing Functions

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Abstract

A meromorphic function on $D \subseteq \mathbb{C}$ is a ratio of analytic functions with denominator identically non zero on D. Poles of such functions arise from zeros in the denominator where the numerator remains non-zero. Determining all poles is a complex task, thus identifying a potential pole region becomes essential. This research aims to establish a pole region for selected meromorphic functions, supported by examples and accompanying figures to validate the findings.

Keywords: Meromorphic function, pole, L-order, L^*-order.

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1. Introduction, Definitions and Notations In 1816, Gauss initially presented a fundamental result concerning the location of zeros of polynomials [7]. Consequently, numerous scholarly articles exploring this topic have been published in the academic literature (cf. [1], [2], [3], [7], [8] & [11]). However, it's important to emphasize that more results of a similar nature for the location of poles of meromorphic functions are not available, except for a limited partial reflection observed in [5].

A meromorphic function $f(z)$ analytic within the annular region defined by $r_1 < |z| < r_2$ can be expressed as $f(z) = \sum_{n\in\mathbb{Z}} a_n z^n$ where $a_n = \frac{1}{2\pi i}\int_\Gamma \frac{f(\xi)}{\xi^{n+1}} d\xi, n \in \mathbb{Z}$ with $\Gamma = \{\xi : |\xi| = r\}$ and $r_1 < r < r_2$.

The primary objective of this paper is to introduce a region that encompasses the poles of a meromorphic function under various conditions, utilizing the coefficients a_n.

It's important to note that this paper does not delve into standard theories, as they are available in references [9] & [15]. The following section provides some well-known definitions for clarity.

***Definition* 1.1. [6]** The Nevanlinna characteristic function $T(r, f)$ for a meromorphic function f in the finite complex plane $\mathbb{C}$ is defined as:

$$T(r,f) = \frac{1}{2\pi}\int_0^{2\pi} \log^+\left|f\left(re^{i\theta}\right)\right| d\theta + \int_0^r \frac{n(t,f)}{t} dt$$

where $n(t, f)$ represents the count of poles of the function f within the region $|z| \le t$ and

$$\log^+ x = \log x \text{ when } x \ge 1$$
$$= 0 \text{ when } 0 \le x \le 1.$$

***Definition* 1.2. [6]** The order of a meromorphic function f is defined by

$$\rho = \limsup_{r\to\infty} \frac{\log T(r,f)}{\log r}.$$

***Definition* 1.3. [4]** For a meromorphic function f having order zero, the quantity ρ^* is defined by

$$\rho^* = \limsup_{r\to\infty} \frac{T(r,f)}{\log r}.$$

***Definition* 1.4. [13]** A continuous function $L(r) > 0$ is said to be inereasing slowly if

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$$\lim_{r\to\infty}\frac{L(ar)}{L(r)}=1\ \forall\ a>0.$$

***Definition* 1.5.** [**14**] For a meromorphic function f, its L-order ρ^L and L^*-order ρ^{L^*} are defined as

$$\rho^L=\limsup_{r\to\infty}\frac{\log\ T(r,f)}{\log\ (rL(r)]}\text{ and }\rho^{L^*}=\limsup_{r\to\infty}\frac{\log\ T(r,f)}{\log\ [re^{L(r)}]}.$$

2. Lemmas

In this section we present some lemmas which will be needed in the sequel.

***Lemma* 2.1**. [**12**] For any complex number c_j with $\left|\arg\ c_j-\delta\right|\le\gamma\le\frac{\pi}{2}$ for some real γ and δ, the following inequality holds:

$$\left|c_j-c_{j-1}\right|\le||c_j|-|c_{j-1}||\cos\ \gamma+\left(\left|c_j\right|+\left|a_{j-1}\right|\right)\sin\ \gamma.$$

***Lemma* 2.2.** [**1**] Let $g(z)$ be andytic in $|z|\le t$ with $g(0)=0, g^J(0)=a$ and $|g(z)|\le K$ for $|z|=t$. Then for $|z|\le t$,

$$|g(z)|\le\frac{K|z|}{t^2}\cdot\frac{K|z|+t^2|a|}{K+|a||z|}.$$

3. Theorems

In this section, we present the main results of our research. These results significantly advance our understanding of the distribution of poles in meromorphic functions, particularly in the context of slowly changing functions. These offer valuable insights and solutions to address the challenges within this field, opening doors for further exploration and practical applications.

***Theorem* 3.1.** Let a meromorphic function $f(z)$ on $D\subseteq\mathbf{C}$ be of finite L-order $\rho^L(\ge1)$ with $f(z)=\sum_{n-0}^{\infty}a_nz^n+\sum_{n=-1}^{-\infty}a_nz^n$ for $R_1\le|z|\le R_2$. Also let for some real numbers γ and δ,

$$\left|\arg\ a_j-\delta\right|\le\gamma\le\frac{\pi}{2},j=0,1,2,\ldots$$

and

$$\rho^L|a_0|\ge R_2|a_1|\ge R_2^2|a_2|\ge\cdots.$$

Then poles of $f(z)$ reside in $D_1\cup D_2$

where $D_1=\left\{z\in D:R_2<|z|\le\frac{BR_2}{|\rho_{a0}-R_2a_1|}\right\},D_2=\{z\in D:|z|<R_1\}$

and $B=(\cos\ \gamma+\sin\ \gamma)\rho^L|a_0|+2\sin\ \gamma\sum_{j=1}^{\infty}\left|a_j\right|R_2$.

Proof. Clearly, $\lim_{n\to\infty}a_nR_2^{\mathrm{n}}=0$ and $\lim_{n\to\infty}a_nR_1^{\mathrm{n}}=0$.

Also, for $R_1<|z|<R_2$, it follows that

$$|f(z)|\le|\textstyle\sum_{n=0}^{\infty}\ a_nz^n|+|\sum_{n=-1}^{\infty}\ a_nz^n|.\quad(1)$$

Now, for $|z|<R_2$, we get that

$$(z-R_2)\textstyle\sum_{n=0}^{\infty}\ a_nz^n$$

$$=-R_2\mathrm{a}_0+(a_0-R_2a_1)z+\textstyle\sum_{j=2}^{\infty}\ \left(a_{j-1}-R_2a_j\right)z^j$$

$$=-R_2a_0+(a_0-\rho^{\mathrm{L}}\mathrm{a}_0+\rho^{\mathrm{L}}\mathrm{a}_0-R_2a_1)z+\textstyle\sum_{j=2}^{\infty}\ \left(a_{j-1}-R_2a_j\right)z^j$$

$$=-R_2a_0+a_0(1-\rho^L)z+(\rho^{\mathrm{L}}\mathrm{a}_0-R_2a_1)z+\textstyle\sum_{j=2}^{\infty}\ \left(a_{j-1}-R_2a_j\right)z^j$$

$$=-R_2a_0+a_0(1-\rho^L)z+G(z).\qquad(2)$$

Using *Lemma* 2.1, it follows for $|z|=R_2$ that

$$|G(z)|\le|\rho^La_0-R_2a_1||z|+\sum_{j=2}^{\infty}\ \left|a_{j-1}-R_2a_j\right||z|^j$$

$$\le|\rho^La_0-R_2a_1|R_2+\textstyle\sum_{j=2}^{\infty}\ \left|a_{j-1}-R_2a_j\right|R_2\le\{|\rho^L|a_0|-R_2|a_1||\cos\gamma+(\rho^L|a_0|+R_2|a_1|)\sin\gamma\}R_2+\sum_{j=2}^{\infty}\left\{\left||a_{j-1}|-R_2|a_j|\right|\cos\gamma+\left(\left|a_{j-1}\right|+R_2\left|a_j\right|\right)\sin\gamma\right\}R_2^j$$

$$=(\rho^L|a_0|-R_2|a_1|)R_2\cos\gamma+(\rho^L|a_0|+R_2|a_1|)R_2\sin\gamma+\textstyle\sum_{j=2}^{\infty}\ \left(\left|a_{j-1}\right|-R_2\left|a_j\right|\right)R_2\cos\gamma$$

$$+\sum_{j=2}^{\infty}\ \left(\left|a_{j-1}\right|+R_2\left|a_j\right|\right)R_2^j\sin\gamma$$

$$= (\cos\gamma + \sin\gamma)\rho^L|a_0|R_2 + 2R_2\sin\gamma\sum_{j=1}^{\infty}|a_j|R_2^j$$

$$= R_2B \text{ where } B = (\cos\gamma + \sin\gamma)\rho^L|a_0| + 2\sin\gamma\sum_{j=1}^{\infty}|a_j|R_2^j.$$

Now, $G(z)$ being analytic in $|z| \le R_2$ with $G(0) = 0, G'(0) = (\rho' a_0 - R_2 a_1)$ and $|G(z)| \le R_2B$ for $|z| = R_2$, we obtain by *Lemma* 2.2 that

$$|G(z)| \le \frac{BR_2|z|}{R_2^2}\cdot\frac{BR_2|z| + R_2^2 \mid \rho^L a_0 - R_2 a_1|}{BR_2 + |\rho^L a_0 - R_2 a_1||z|}$$

$$= \frac{B|z|\{B|z| + R_2|\rho^L a_0 - R_2 a_1|\}}{BR_2 + |\rho^L a_0 - R_2 a_1 \parallel z|}.$$

Hence for $|z| < R_2$, we get from (2) that

$$\left|(z - R_2)\sum_{n=0}^{\infty} a_n z^n\right|$$

$$\le |-R_2 a_0 + a_0(1-\rho^L)z| + \frac{B|z|\{B|z| + R_2|\rho^L a_0 - R_2 a_1|\}}{BR_2 + |\rho^L a_0 - R_2 a_1||z|}$$

$$\le \frac{(R_2|a_0| + |a_0|(\rho^L - 1)|z|)(BR_2 + |\rho^L a_0 - R_2 a_1||z|) + B|z|\{B|z| + R_2|\rho^L a_0 - R_2 a_1|\}}{BR_2 + |\rho^L a_0 - R_2 a_1||z|}$$

Therefore,

$$\left|\sum_{n=1}^{\infty} a_n z^n\right| \le \frac{(R_2|a_0| + |a_0|(\rho^L - 1)|z|)(BR_2 + |\rho^L a_0 - R_2 a_1||z|) + B|z|\{B|z| + R_2|\rho^L a_0 - R_2 a_1|\}}{(R_2 - |z|)(BR_2 + |\rho^L a_0 - R_2 a_1||z|)}$$

$$\le \frac{(R_2|a_0| + |a_0|(\rho^L - 1)|z|)(BR_2 + |\rho^L a_0 - R_2 a_1||z|) + B|z|\{B|z| + R_2|\rho^L a_0 - R_2 a_1|\}}{(R_2 - |z|)(BR_2 - |\rho^L a_0 - R_2 a_1|z\,|)}. \quad (3)$$

Again, for $|z| > R_1$, we have

$$|(a - R_1)\textstyle\sum_{n=-1}^{-\infty} a_{a^2} a^n|$$

$$= \left|a_{-1} + (a_{-2} - R_1 a_{-1})\frac{1}{z} + (a_{-3} - R_1 a_{-2})\frac{1}{z^2} + \cdots\right|$$

$$\le |a_{-1}| + |(a_{-2} - R_1 a_{-1})|\left|\frac{1}{z}\right| + |(a_{-3} - R_1 a_{-2})|\left|\frac{1}{z}\right|^2 + \cdots$$

$$\le |a_{-1}| + (|a_{-2}| + R_1|a_{-1}|)\frac{1}{R_1} + (|a_{-3}| + R_1|a_{-2}|)\frac{1}{R_1} + \cdots$$

$$= 2\left(|a_{-1}| + \frac{|a_{-2}|}{R_1} + \frac{|a_{-3}|}{R_1^2} + \cdots\right)$$

$$= 2R_1\textstyle\sum_{n=-1}^{-\infty}|a_n|R_1^n = C.$$

Therefore, for $|z| > R_1$,

$$\left|\sum_{n=-1}^{-\infty} a_{n^2} z^n\right| \le \frac{C}{|z| - R_1} \quad (4)$$

Hence, by using (3) and (4), for $R_1 < |z| < R_2$ it follows

from (1) that

$$|f(z)| \le \frac{\left[\begin{matrix}(R_2|a_0| + |a_0|(\rho^L - 1)|z|)(BR_2 + |\rho^L a_0 - R_2 a_1||z|) \\ +B|z|\{B|z| + R_2|\rho^L a_0 - R_2 a_1|\}\end{matrix}\right]}{(R_2 - |z|)(BR_2 - |\rho^L a_0 - R_2 a_1||z|)} + \frac{C}{|z| - R_1}$$

$$\le \frac{\left[\begin{matrix}(|z| - R_1)\{(R_2|a_0| + |a_0|(\rho^L - 1)|z|)(BR_2 + |\rho^L a_0 - R_2 a_1||z|) \\ +B|z|(B|z| + R_2|\rho^L a_0 - R_2 a_1|)\} \\ +C(R_2 - |z|)(BR_2 + |\rho^L a_0 - R_2 a_1 \parallel z|)\end{matrix}\right]}{(R_2 - |z|)(BR_2 - |\rho^L a_0 - R_2 a_1||z|)(|z| - R_1)}.$$

Therefore,

$$\frac{1}{|f(z)|} > 0 \text{ if } (R_2 - |z|)(BR_2 - |\rho^L a_0 - R_2 a_1| \cdot |z|)(|z| - R_1) > 0.$$

Now, for $|z| > R_2$, it follows that $\frac{1}{|(z)} > 0$ if $(BR_2 - |\rho^L a_0 - R_2 a_1|.|z|) < 0$

$$\text{i.e., } \frac{1}{|f(z)\,|} > 0 \text{ if } |z| > \frac{BR_2}{|\,\rho^L a_0 - R_2 a_1|}.$$

Hence zeros of $\frac{1}{f(z)}$ reside in

$$R_2 < |z| \le \frac{BR_2}{|\rho^L a_0 - R_2 a_1|}.$$

As $f(z)$ is analytic in $R_1 \le |z| \le R_2$, poles of $f(z)$ lie in $D_1 = \left\{z \in D: R_2 < |z| \le \frac{BR_3}{|\rho^L a_0 - R_2 a_1|}\right\}$.
Now, for $|z| < R_1 < R_2$, we se that

$$\frac{1}{|f(z)|} > 0 \text{ if } (BR_2 - |\rho^L a_0 - R_2 a_1||z|) < 0.$$

Consequently, poles of $f(z)$ reside in $D_2 = \{z \in D: |z| < R_1\}$.
Combining both the cases $D_1 \cup D_2$ is the region of poles of $f(z)$.

■

Remark 3.1. Taking $f(z)$ as a rational function and $L(r) = \log r, \rho^L = 0$. On the other hand, $\rho^* \ge 1$. Keeping all these in mind, the following theorem may state for meromorphic functions with $\rho^L = 0$.

***Theorem* 3.2.** Let a meromorphic function $f(z)$ on $D \subseteq \mathbb{C}$ be of finite order $\rho^*(\ge 1)$ and $f(z) = \sum_{n=0}^{\infty} a_n z^n + \sum_{n=-1}^{-\infty} a_n z^n$ for $R_1 \le |z| \le R_2$. Also let for some real numbers γ and δ,

$$|\arg\ a_j - \delta| \le \gamma \le \frac{\pi}{2}, j = 0,1,2, \dots$$

and

$$\rho^* |a_0| \ge R_2 |a_1| \ge R_2^2 |a_2| \ge \cdots$$

Then poles of $f(z)$ reside in $D_1' \cup D_2'$
where $D_1' = \left\{z \in D: R_2 < |z| \le \frac{B' R_2}{|\rho^* a_0 - R_2 a_1|}\right\}, D_2' = \{z \in D: |z| < R_1\}$
and $B' = (\cos\gamma + \sin\gamma)\rho^* |a_0| + 2\sin\gamma \sum_{j=1}^{\infty} |a_j| R_2^j$.

Theorem **3.2** can be proved as Theorem 3.1 and therefore its proof is excluded.

***Remark* 3.2**. The following example with related figure ensures the validity of Theorem 3.2.

***Example* 3.1**. Let

$$f(z) = \frac{1}{(z+i)(z+2i)(z+5)}.$$

Now for $2 < |z| < 5$, the Laurent's series expansion of $f(z)$ is

$$f(z) = \frac{23+15i}{29\times26\times5} - \frac{23+15i}{29\times26\times5^2} z + \frac{23+15i}{29\times26\times5^3} z^2 - \cdots + \frac{81-15i}{29\times26}\frac{1}{z} + \frac{115+75i}{29\times26}\frac{1}{z^2} + \cdots$$

Here,

$$a_0 = \frac{28+154}{23\times26\times5}, \quad a_1 = -\frac{23+154}{23\times26\times5^2}$$

and $\rho^* = 3$.
Taking $R_1 = 2.5$, $R_2 = 4$, $\gamma = \frac{\pi}{2}$ and $\delta = 0$, we see that all the conditions of Theorem 3.2 are satisfied.

Now,

$$B' = (\cos\gamma + \sin\gamma)\rho^* |a_0| + 2\sin\gamma \sum_{j=1}^{\infty} |a_j| R_2^j$$
$$= \frac{3}{29\times26\times5}|23+15i| + \frac{2}{29\times26\times5}|23+15i| \sum_{j=1}^{\infty} \left(\frac{4}{5}\right)^j \approx 0.08$$
and $|\rho^* a_0 - R_2 a_1| = \left|3\frac{23+15i}{29\times26\times5} + 4\frac{23+15i}{29\times26\times5^2}\right| \approx 0.028.$

Hence by Theorem 3.2, poles of $f(z)$ reside in

$$\{z \in \mathbb{C}: |z| < 2.5\} \cup \{z \in \mathbb{C}: 4 < |z| \le 11.43\}.$$

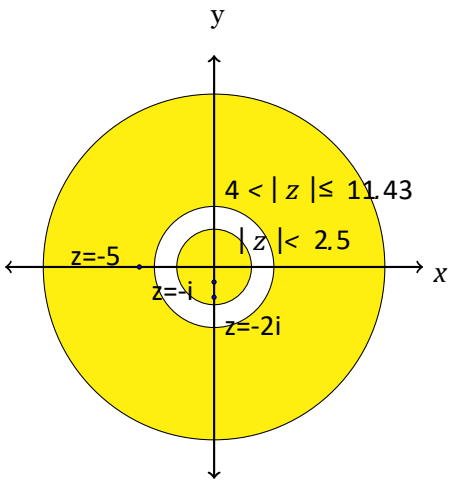

Figure 1: Distribution of the poles of $f(z) = \frac{23+15i}{29\times26\times5} - \frac{23+15i}{29\times26\times5^2} z + \frac{23+15i}{29\times26\times5^3} z^2 - \cdots + \frac{81-15i}{29\times26}\frac{1}{z} + \frac{115+75i}{29\times26}\frac{1}{z^2} + \cdots$

Continuing the discussion, the next theorem focuses solely on the real part of the coefficients of the analytic part of the Laurent series expansion of meromorphic functions.

***Theorem* 3.3.** Let a meromorphic function $f(z)$ on $D \subseteq \mathbb{C}$ be of finite L-onder $\rho^L(\ge 1)$ with

$f(z) = \sum_{n=0}^{\infty} a_n z^n + \sum_{n=-1}^{-\infty} a_n z^n$ for $R_1 \leq |z| \leq R_2$. If $a_j = \alpha_j + i\beta_j, j = 0,1,2, \ldots$ and

$$0 < \rho^L \alpha_0 \geq R_2 \alpha_1 \geq R_2^2 \alpha_2 \geq \cdots$$

Then $D_3 \cup D_4$ is the region of poles of $f(z)$

where $D_3 = \left\{ z \in D : R_2 < |z| \leq \frac{MR_2}{\rho^L \alpha_0 - R_2 \alpha_1} \right\}$, $D_4 = \{ z \in D : |z| < R_1 \}$

and $M = \rho^L \alpha_0 + 2 \sum_{j=1}^{\infty} |\beta_j| R_2^j$.

Proof. Clearly, $\lim_{j \to \infty} \alpha_j R_2^{\,j} = 0$, $\lim_{j \to \infty} \beta_j R_2^{\,j} = 0$

and $\lim_{j \to -\infty} a_j R_1^{\,j} = 0$.

Now, for $|z| < R_2$, it follows that

$$(z - R_2) \sum_{n=0}^{\infty} a_n z^n = -R_2 a_0 + (a_0 - R_2 a_1) z + \sum_{j=2}^{\infty} (a_{j-1} - R_2 a_j) z^j$$

$$= -R_2 a_0 + (\alpha_0 - R_2 \alpha_1) z + i(\beta_0 - R_2 \beta_1) z + \sum_{j=2}^{\infty} \{(\alpha_{j-1} - R_2 \alpha_j) + i(\beta_{j-1} - R_2 \beta_j)\} z^j$$

$$= -R_2 a_0 + (\alpha_0 - \rho^L \alpha_0 + \rho^L \alpha_0 - R_2 \alpha_1) z + i(\beta_0 - R_2 \beta_1) + \sum_{j=2}^{\infty} \{(\alpha_{j-1} - R_2 \alpha_j) + i(\beta_{j-1} - R_2 \beta_j)\} z^j$$

$$= -R_2 a_0 + (1 - \rho^L) \alpha_0 z + (\rho^L \alpha_0 - R_2 \alpha_1) z + i(\beta_0 - R_2 \beta_1) z + \sum_{j=2}^{\infty} \left\{ \left(\alpha_{j-1} - R_{2\alpha_j}\right) + i(\beta_{j-1} - R_2 \beta_j) \right\} z^j$$

$$= -R_2 \alpha_0 + (1 - \rho^L) \alpha_0 z + H(z). \quad (1)$$

For $|z| = R_2$, we have

$$|H(z)| \leq |\rho^L \alpha_0 - R_2 \alpha_1 ||z| + |\beta_0 - R_2 \beta_1 ||z| + \sum_{j=2}^{\infty} |\alpha_{j-1} - R_2 \alpha_j ||z|^j + \sum_{j=2}^{\infty} |\beta_{j-1} - R_2 \beta_j ||z|^j$$

$$\leq (\rho^L \alpha_0 - R_{2\alpha_1}) R_2 + (|\beta_0| + R_2 |\beta_1|) R_2 + \sum_{j=2}^{\infty} (\alpha_{j-1} - R_2 \alpha_j) R_2 + \sum_{j=2}^{\infty} (|\beta_{j-1}| + R_2 |\beta_j|) R_2$$

$$= \rho^L \alpha_0 R_2 + R_2 |\beta_0| + 2R_2 \sum_{j=1}^{\infty} |\beta_j| R_2^j$$

$$= MR_2 \text{ where } M = \rho^L \alpha_{\alpha_0} + |\beta_0| + 2 \sum_{j=1}^{\infty} |\beta_j| R_2^j.$$

As $H(z)$ is analytic in $|z| \leq R_2$ with $H(0) = 0, H'(0) = (\rho^L \alpha_0 - R_2 \alpha_1)$ and $|H(z)| \leq R_2 M$ for $|z| = R_2$, we get by Lemma 2.2 that

$$|H(z)| \leq \frac{MR_2|z|}{R_2^2} \cdot \frac{MR_2|z| + R_2^2 |\rho^L \alpha_0 - R_2 \alpha_1|}{MR_2 + |\rho^L \alpha_0 - R_2 \alpha_1| |z|} = \frac{M|z|\{M|z| + R_2(\rho^L \alpha_0 - R_2 \alpha_1)\}}{MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z|}$$

Hence for $|z| < R_2$, it follows from (1) thut

$$|(z - R_2) \sum_{n=0}^{\infty} a_n z^n| \leq |-R_2 a_0 + (1 - \rho^L) \alpha_0 + \frac{M|z|\{M|z| + R_2(\rho^L \alpha_0 - R_2 \alpha_1)\}}{MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z|}$$

$$\leq R_2 |a_0| + (\rho^L - 1) \alpha_0 |z| + \frac{M|z|\{M|z| + R_2(\rho^L \alpha_0 - R_2 \alpha_1)\}}{MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z|}$$

$$= \frac{\{R_2|a_0| + (\rho^L - 1)\alpha_0|z|\}\{MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z|\} + M|z|\{M|z| + R_2(\rho^L \alpha_0 - R_2 \alpha_1)\}}{MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z|}$$

Therefore,

$$\left| \sum_{n=0}^{\infty} a_n z^n \right| \leq \frac{\{R_2|a_0| + (\rho^L - 1)\alpha_0|z|\}|MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z\,|\} + M|z|\{M|z| + R_2(\rho^L \alpha_0 - R_2 \alpha_1)\}}{(R_2 - |z|)\{MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z|\}}$$

$$\leq \frac{\{R_2|a_0| + (\rho^L - 1)\alpha_0|z|\}|MR_2 + (\rho^L \alpha_0 - R_2 \alpha_1)|z\,|\} + M|z|\{M|z| + R_2(\rho^L \alpha_0 - R_2 \alpha_1)\}}{(R_2 - |z|)\{MR_2 - (\rho^L \alpha_0 - R_2 \alpha_1)|z|\}} \quad (2)$$

Now, for $|z| > R_1$, we get from (4) of Theorem 3.1 that

$$\left| \sum_{n=-1}^{-\infty} a_n z^n \right| \leq \frac{C}{|z| - R_1} \text{ where } C = 2R_1 \sum_{n=-1}^{-\infty} |a_n| R_1^n. \quad (3)$$

Hence, we obtain for $R_1 < |z| < R_2$ that

$$|f(z)| \leq \left|\sum_{n=0}^{\infty} a_n z^n\right| + \left|\sum_{n=-1}^{-\infty} a_n z^n\right|$$

$$\leq \frac{\{R_2|a_0| + (\rho^L - 1)\alpha_0|z|\}\{MR_2 + (\rho^L\alpha_0 - R_2\alpha_1)|z|\} + M|z|\{M|z| + R_2(\rho^L\alpha_0 - R_2\alpha_1)\}}{(R_2 - |z|)\{MR_2 - (\rho^L\alpha_0 - R_2\alpha_1)|z|\}} + \frac{C}{|z| - R_1}$$

$$\leq \frac{(|z| - R_1)[\{R_2|a_0| + (\rho^L - 1)\alpha_0|z|\}\{MR_2 + (\rho^L\alpha_0 - R_2\alpha_1)|z|\} + M|z|\{M|z| + R_2(\rho^L\alpha_0 - R_2\alpha_1)\}] + C(R_2 - |z|)(MR_2 - (\rho^L\alpha_0 - R_2\alpha_1)|z|)}{(|z| - R_1)(R_2 - |z|)\{MR_2 - (\rho^L\alpha_0 - R_2\alpha_1)|z|\}} \cdot f(z) \quad (4)$$

From (4), we see that

$$\frac{1}{|f(z)|} > 0 \text{ if } (|z| - R_1)(R_2 - |z|)\{MR_2 - (\rho^L\alpha_0 - R_2\alpha_1)|z|\} > 0.$$

Now, for $|z| > R_2$,

$$\frac{1}{|f(z)|} > 0 \text{ if } MR_2 - (\rho^L\alpha_0 - R_2\alpha_1)|z| < 0$$

$$\text{i.e., } \frac{1}{|f(z)|} > 0 \text{ if } |z| > \frac{MR_2}{\rho^L\alpha_0 - R_1\alpha_1}.$$

Hence zeros of $\frac{1}{f(z)}$ reside in $R_2 < |z| \leq \frac{MR_2}{\rho^L\alpha_0 - R_1\alpha_1}$ and consequently poles of $f(z)$ in $R_2 < |z| \leq \frac{MR_2}{\rho^L\alpha_0 - R_1\alpha_1}$.

Also, for $|z| < R_1 < R_2$,

$$\frac{1}{|f(z)|} > 0 \text{ if } \{MR_2 - (\rho^L\alpha_0 - R_2\alpha_1)|z|\} < 0.$$

Therefore, poles of $f(z)$ reside in $|z| < R_1$. Thus the theorem is established. ■

The forthcoming theorem shares similarities with the previous one and is applicable to meromorphic functions with $\rho^L = 0$.

***Theorem* 3.4.** Let a meromorphic function $f(z)$ on $D \subseteq \mathbb{C}$ be of finite order $\rho^*(\geq 1)$ and $f(z) = \sum_{n=0}^{\infty} a_n z^n + \sum_{n=-1}^{-\infty} a_n z^n$ for $R_1 \leq |z| \leq R_2$. If $a_j = \alpha_j + i\beta_j, j = 0, 1, 2, \ldots$ and

$$0 < \rho^*\alpha_0 \geq R_2\alpha_1 \geq R_2^2\alpha_2 \geq \cdots$$

Then poles of $f(z)$ reside in $D_3' \cup D_4'$

where $D_3' = \left\{z \in D: R_2 < |z| \leq \frac{M'R_2}{\rho^*\alpha_0 - R_2\alpha_1}\right\}, D_4' = \{z \in D: |z| < R_1\}$ and $M' = \rho^*\alpha_0 + 2\sum_{j=1}^{\infty} |\beta_j| R_2^j$.

The proof is similar to Theorem 3.3.

***Remark* 3.3**. The following example with related figure justifies the validity of Theorem 3.4.

***Example* 3.2**. Let

$$f(z) = \frac{1}{(z-1)(z-2)(3-z)}.$$

Now, for $2 < |z| < 3$, the Laurent's series expansion of $f(z)$ is

$$f(z) = \frac{1}{6} + \frac{1}{18}z + \frac{1}{54}z^2 + \cdots + \frac{1}{2z} + \frac{3}{2z^2} + \cdots$$

Here, $R_1 = 2.01, R_2 = 2.99,\ \alpha_0 = \frac{1}{6},\ \alpha_1 = \frac{1}{18}$ and $\rho^* = 3$.

Now,

$$M' = \rho^*\alpha_0 + 2\sum_{j-1}^{\infty} |\beta_j| R_2^j = \frac{1}{2} \quad \text{and} \quad \frac{M'R_2}{\rho^*\alpha_0 - R_2\alpha_1} \approx 4.48$$

Hence by Theorem 3.4, the region for poles of $f(z)$ is

$$\{z \in \mathbb{C}: |z| < 2.01\} \cup \{z \in \mathbb{C}: 2.99 < |z| \leq 4.48\}.$$

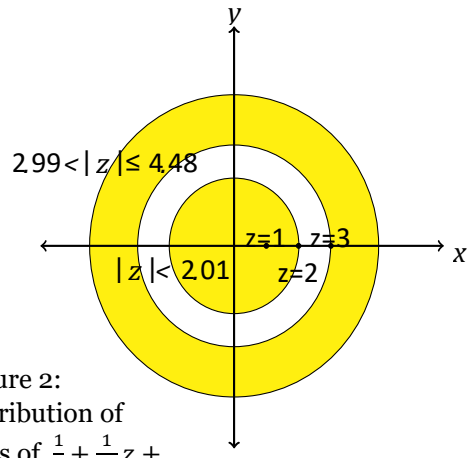

Figure 2: Distribution of poles of $\frac{1}{6} + \frac{1}{18}z + \frac{1}{54}z^2 + \cdots + \frac{1}{2z} + \frac{3}{2z^2} + \cdots$

***Remark* 3.4**. Theorem 3.1 and Theorem 3.3 are also valid for meromorphic functions with $\rho^{L^*} \geq 1$.

Future prospect.

In the line of the works as carried out in the paper one may think of proving the results in case of meromorphic functions having infinite L^*-order.

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Exploring Aromaticity: From Linear Polyacene to Helicene

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Abstract

We have computationally studied the aromaticity of a series of polyacenes, from linear to bent and/or helical polyacenes, keeping the total number of carbon atoms intact. The traditional structure-based aromaticity index (HOMA) has been correlated with the Clar 2-nomial for each polyacene. We have found that linear polyacenes are less aromatic than angular ones. Some other related parameters, like the HOMO-LUMO gap, the average NICS values, etc., are also computed to investigate the aromaticity involved in these types of systems. We have found that the structure-based aromaticity indices go parallel with the graph-based aromaticity indices.

Keywords: Aromaticity; Linear Polyacene; Helicene; HOMA; NICS

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1. Introduction

In the early 19th century, the term "aromaticity" was mostly employed to describe a certain class of organic substances in a chemical sense.[1,2] It is still crucial to the rationalization of the structure, stability, and reactivity of many molecules in the discipline of physical organic chemistry. The scientific community is still baffled by aromaticity because there is not a single definition for it and it has multiple dimensions. On the other hand, characteristics such as (i) planarity, (ii) total (4n + 2)π electrons, (iii) stabilization energy,[3-4] (iv) bond length,[5] (v) magnetic exaltation,[6] (vi) preservation of π-electron delocalization after typical reactions,[7] and so on can be used to quantify aromaticity. All of the aforementioned traits are present in a completely aromatic system. Due to its multidimensional nature and lack of a single, definitive definition, aromaticity is quantified using a variety of indices. One such structural indices is the harmonic oscillator model of aromaticity (HOMA), which can accurately describe the variations in aromaticity in more complex systems.[8] The indices based on geometry When bond length alternation and rise, The geometry based quantifier HOMA quantifies the reduction in aromaticity with the increase in the bond length alternation and subsequent bond elongation.[9] Not only can aromaticity be illustrated by geometry based indices like HOMA but also a specified π-electron part in some greater π-electron structure may be affected by its structural environment.[8-10]

Beside HOMA index, nucleus independent chemical shift (NICS) is another widely used

index of aromaticity because of its simplicity and efficiency.[11-13] The extent of aromaticity can be established experimentally by the 1H NMR shift of aromatic and anti-aromatic compounds. This effect is a consequence of the π-electron ring current of aromatic systems under the influence of external magnetic field. NICS can be widely used to identify aromaticity, non-aromaticity, and anti-aromaticity of a single ring system and individual ring in polycyclic systems (local aromaticity).

In their landmark work on the "Nature of Chemical Bond," Pauling and Wheland succeeded in presenting a quantitative resonance theoretical picture of the graphitic network in a practical, chemically suitable, and quantitative form in 1939.[14] Nearly forty years later, Clar presented his theories in a brief pamphlet on "aromatic sextet" theory, which provides a qualitative explanation for the stability of conjugated systems.[15] The spectrum of benzenoid systems served as an illustration of his views on the aromatic sextet. Herndon and Hosoya have used the Clar structures for benzenoid hydrocarbons to parameterize valence bond computations, although Clar's concepts characterized the aromaticity of benzenoid hydrocarbons through the experimental method.[16] In 1976, Randić proposed the "conjugated circuit model" to analyze the aromaticity of conjugated polycyclic compounds, drawing inspiration from Clar structures.[17] Using the model, it was established that the Helicenes are relatively more stable than equivalent polyacenes.[18] Cyvin and Gutman have previously published a list of numerous formulas in their book[19] that may be used to count the number of Kekule structures K (B) for different kinds of benzenoid systems (B). In a different study, Klien et al. examined a qualitative resonance theoretical approach to explain the characteristics of π-electron spins on different kinds of graphitic network boundaries.[20,21] Klein's method took into account the pairing of adjacent neighboring (starred or unstarred) and non-neighboring (unstarred or starred) sites of various graphitic edges.[22] The numbers (χ_n^*) of starred sites of degree n and the numbers (χ_n^0) of unstarred sites of degree n were used to indicate the overall ground state spin:

$$S_{RT=}|2\chi_1^* + \chi_2^* - 2\chi_1^0 - \chi_2^0|/6 \quad (1)$$

Later the resonance theoretically anticipated ground state spin was re-expressed in terms of the total numbers of starred and unstarred sites, or χ^* and χ^0.as

$$S_{\mathrm{RT}} = |\chi^* - \chi^0|/2 \quad (2)$$

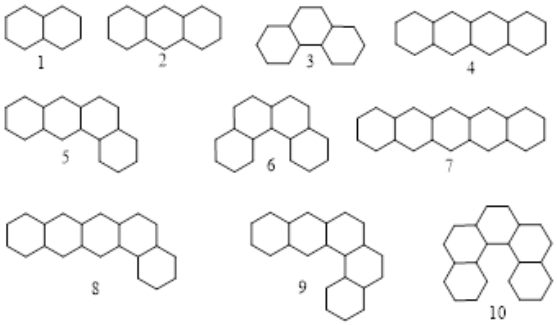
The wide strip systems with two well-separated edges showed good agreement between the unrestricted HF computations and this variety of simple resonance theoretic predictions for edge localized electrons. In 2009 Misra and co-worker extended Eric Clar's ideas about "aromatic sextet" to a quantitative format in terms of "Clar 2-nomial" considering molecular benzenoids[22] and subsequently radical benzenoids.[23] Clar's theory has been effectively used to conjugated carbon nanostructures, such as carbon nanotubes,[24] nanoribbons,[25] etc., as a part of the theoretical development involved. By employing density functional theory calculations, Baldoni et al. were able to justify their use of the theory in obtaining edge energies, band gap, and edge-induced stresses of hydrogen terminated graphene nanoibbons.[26] King and Ormsby have

examined the electrical structure and magnetic characteristics of flawless single-walled carbon nanotubes using Clar's valence bond model in a different study.[24] Apart from graphene, defective graphene, carbon nanotubes, nanoribbon, and diverse types of fullerenes, verities of conjugated carbon nanostructure such as, fractal benzenoids, nano-tori, nano-cone was also defined by Clar's concepts.[27]

As the number of rings increases, linear polyacenes become more reactive, making it impossible to experimentally characterize the higher members.[15, 16] The inner rings are where major chemical processes preferentially take place. Another illustration of monotonic behaviour in the polyacene series is the progressive narrowing of the gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).[28, 29] The aromaticity of each ring changes when a linear polyacene is converted to a bent polyacene.

In this work we have studied the nature of change of aromaticity with the change in the structure (from linear to angular) of polyacene molecules with same number of carbon atoms, namely, (1) naphthalene (2) anthracene and (3) phenanthrene; (4) tetracene, (5) benzanthracene, (6) benzo[c] phenanthrene, (7) pentacene, (8) benzo[a]naphthacene, (9) naphtha[1,2-α] anthracene and (10) Dibenzo [c,g] phenanthrene (Figure 1). We have studied the local aromaticity of individual rings in terms of structural aromaticity index HOMA, nucleus independent chemical shift, NICS(0) and NICS(I), and the graph based aromaticity index, Clar's Aromaticity Index (Clar 2-nomial). We have also compared the HOMO-LUMO gap, electronegativity and hardness of the linear and angular polyacene to study their aromatic nature in terms of these parameteres.

Figure 1. The polyacene compounds under study. For simplicity, the double bond and/or rings showing the delocalization of electrons are avoided. Only the schematic molecular



graphs are shown.

2. Theoretical and Computational Detail

The local aromaticity of polyacene compounds can be investigated using the Harmonic Oscillator Model of Aromaticity (HOMA) index.[30-36] It is one of the most accurate structural measures of local aromaticity. The HOMA index for each benzene ring in a polycyclic aromatic hydrocarbon molecule is defined as[30-35]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{6}\sum_{i=1}^{6}(R_0 - R_i)^2 \qquad (3)$$

where α and R are the constants characteristic of C-C bonds in a hydrocarbon π-system, R_i is the observed or calculated length of the i^{th} C-C bond in a given benzene ring and the summation is made over the six π-bonds. A large positive HOMA value indicates a larger degree of local aromaticity in the ring concerned. We adopted the values α=257.7 and R_0=1.388 Å [37] to calculate HOMA indices.

The electronegativity (χ) and hardness (η) in terms energy of HOMO and LUMO can be written as

$$\chi = -\frac{E_{HOMO} + E_{LUMO}}{2} \qquad (4)$$

and

$$\eta = E_{HOMO} - E_{LUMO} \qquad (5)$$

All the molecular geometries have been optimized using restricted B3LYP functional and 6-31+G(d,p) basis set.

The NICS values of the non-chemical probe 'Bq" are computed on the ring plane

[NICS(0)]. Nonetheless, the influence of the π-system's interaction with the σ-skeleton of the relevant ring is intrinsically included in the NICS(0) values. Therefore, NICS values are also computed 1 Å atop the ring [NICS(1)] of the systems under study to assess the local aromaticity. The aromaticity index NICS of the polyacenes has been estimated by using UB3LYP/GIAO methodology with 6-31+G(d,p) basis set. The GIAO method [38] was used to perform calculations of NICS values at the centre of the rings (NICS(0)). All the calculations have been done using Gaussian09 suite of programme.[39]

A brief discussion on Quantitative Clar Theory is due here. The theory, developed by Klein et. al., is essentially based on valence structures[40] with conjugated π –network in each site that is indicated to either a Clar sextet or a double bond.[41] Thus a Clar structure is a classical electronic structure that contain Clar sextet in one ring and an arrow is interconnected to the adjacent ring containing two double bonds. Thus the Clar structure describes the π-network identified by graph B and subsequently one can construct the Clar polynomial P of various systems following the earlier work[22,23,40]

$$P_B(x,y) \equiv \sum_C^B x^{s_B(C)}\, y^{a_B(C)} \qquad (6)$$

The terms x and y in this polynomial denote the contribution of Clar sextets and the arrow that connects them to their neighboring ring, respectively. The varied weights of the several Clar structures connected to Clar structure C can be added to form the total. The number of Clar sextets in C and the number of rings next to the Clar sextet into which a Clar sextet can move with the least amount of bond rearrangement—that is, the degree of mobility to the Clar sextet—are indicated by the symbols s_G (C) and a_G(C) in Clar structures. In keeping with our prior work, we employ the variables x = 2 and y = 1 in this work.[22,23] We discuss the Clar aromaticity index adopting a similar treatment as was done in our previous work for quantifying local aromaticity. Klein et al. have shown that the Clar aromaticity Index (CAI) for a hexagonal ring κ of a benzenoid B can be expressed as

$$CAI_B(\kappa) = \sum_C^B s_B(C,\kappa) x^{s_B(C)} y^{a_B(C)} / P_B(x,y) \quad (7)$$

$$CAI'_B(\kappa) = \sum_C^B a_B(C,\kappa) x^{s_B(C)} y^{a_B(C)} / P_B(x,y) \quad (8)$$

where $s_B(C,\kappa)$ is 1 or 0 depending on whether κ is in Car sextet in C or not. Also, $a_B(C,\kappa)$ counts the number of naphthalenes which contains $\kappa \subseteq C$ along with two other double bonds of naphthalene contained in C. Here $CAI'_B(\kappa)$ plays the role of secondary aromaticity index arising from the migration of the sextet to neighboring ring. It can be easily seen that $a_B(C,\kappa)$ is either 0 or 1. These local invariants and the global invariants are connected via $\sum_\kappa^B s_B(C,\kappa) = s_B(C)$ and $\sum_\kappa^B a_B(C,\kappa) = a_B(C)$ which follows

$$\langle s\rangle_B = \sum_\kappa^B CAI_B(\kappa) \quad \text{and} \quad \langle a\rangle_B = \sum_\kappa^B CAI'_B(\kappa) \qquad (9)$$

Hence one can think of expressing local aromaticity of any ring of the polyacene by a linear combination of sextetness ($CAI_B(\kappa)$ and sextet mobility ($CAI'_B(\kappa)$) for that particular ring. Taking into account the non-local contributions as considered in Ref. 22, one can express the Clar aromaticity index (CAI) in terms of three-parameter expression such as

$$CAI(m) = C_1 CAI_G(m) + C_2 CAI'_G(m) + C_3 \frac{1}{1+(n_m/6)} \qquad (10)$$

where n_κ is the number of benzene ring which are adjacent to ring κ. The relevance for introducing the third term can be understood

when one fits the aromaticity index against the non-local contributions from the neighbouring sites.

3. **Results and Discussions**

In this study we have calculated the aromaticity index HOMA, NICS(0) and NICS(1) of different linear polyacene under consideration and their corresponding angular isomer (1-10). The values of HOMA, NICS (0) and NICS (1) for individual rings and their average are shown in **Table 1**.

Table 1. The values of HOMA, NICS(0), NICS(1) and their average of the compounds

Compound	Ring	A	B	C	D	E	Average
1	HOMA	0.76	0.76				0.76
	NICS(0)	– 8.50	– 8.49				– 8.50
	NICS(1)	– 10.37	–10.37				– 10.37
2	HOMA	0.60	0.68	0.60	---		0.63
	NICS(0)	–7.52	–11.19	–7.52	---		–8.74
	NICS(1)	–9.53	–12.55	–9.53	---		–10.54
3	HOMA	0.84	0.42	0.84	---		0.70
	NICS(0)	–8.81	–5.50	–8.81	---		–7.71
	NICS(1)	–10.68	–7.97	–10.68	---		–9.78
4	HOMA	0.51	0.59	0.59	0.51		0.55
	NICS(0)	–6.73	–11.02	–11.02	–6.73		–8.88
	NICS(1)	–8.85	–12.39	–12.39	–8.85		–10.62
5	HOMA	0.72	0.25	0.87	0.68		0.63
	NICS(0)	–8.65	–3.59	–10.35	–8.32		–7.73
	NICS(1)	–10.51	–6.37	–12.0	–10.23		–9.78
6	HOMA	0.76	0.30	0.30	0.76		0.53
	NICS(0)	–9.35	–6.73	–6.73	–9.35		–8.04
	NICS(1)	–10.92	–8.64	–8.64	–10.92		–9.78
7	HOMA	0.47	0.53	0.54	0.53	0.47	0.51
	NICS(0)	–5.86	–10.73	– 12.22	– 10.73	– 5.84	–9.08
	NICS(1)	– 8.09	–12.14	– 13.50	– 12.26	– 8.33	–10.86
8	HOMA	0.55	0.65	0.60	0.16	0.88	0.57
	NICS(0)	–7.22	–11.99	–10.33	–2.65	–8.48	–8.13
	NICS(1)	–9.33	–13.22	–11.94	–5.62	–10.29	–10.08
9	HOMA	0.68	0.69	0.30	0.53	0.78	0.60
	NICS(0)	–8.08	–11.03	–4.28	–6.93	–8.31	–7.73
	NICS(1)	–11.24	–11.99	–6.92	–9.30	–12.92	–10.47
10	HOMA	0.81	0.44	0.58	0.44	0.81	0.62
	NICS(0)	–8.39	–6.09	–6.34	–6.09	–8.39	–7.06
	NICS(1)	–11.29	–7.84	–9.06	–7.68	–11.29	–9.43

The most significant Kekulé resonance structure for describing the characteristics of polycyclic aromatic hydrocarbons (PAHs) is, in accordance with Clar's idea, the one having the greatest number of disjoint aromatic π-sextets, or benzene-like moieties. Six π-electrons located in a single benzene-like ring and isolated from neighbouring rings by formal C-C single bonds have been referred to as aromatic π-sextets. Considering naphthalene (**1**) being a well-studied case, we discuss the aromaticity of anthracene and others (**2-10)**. All the possible Clar structures are shown in **Figure 2**. It is evident that for anthracene the π-electrons are distributed over the three rings equally i.e. all the rings should have equal aromaticity. But from the HOMA and NICS values we conclude that the middle ring is more aromatic than those at the sides.[42] Although it is observed that the higher aromaticity of the central ring of the molecule as indicated by NICS agrees with the stronger ring currents around the inner rings of acenenes.[43] On the other hand phenanthrene which is an isomer of anthracene contains two aromatic sextet in the terminal and consequently they have higher values of NICS and HOMA than central one. The average HOMA value of phenanthrene is higher than that of anthracene. This can be explained as anthracene contains one Clar sextet in its resonance structure but phenanthrene contains two sextets. On the other hand average NICS values show opposite trend, this is because of the sextet migration is impossible for phenanthrene.[22]

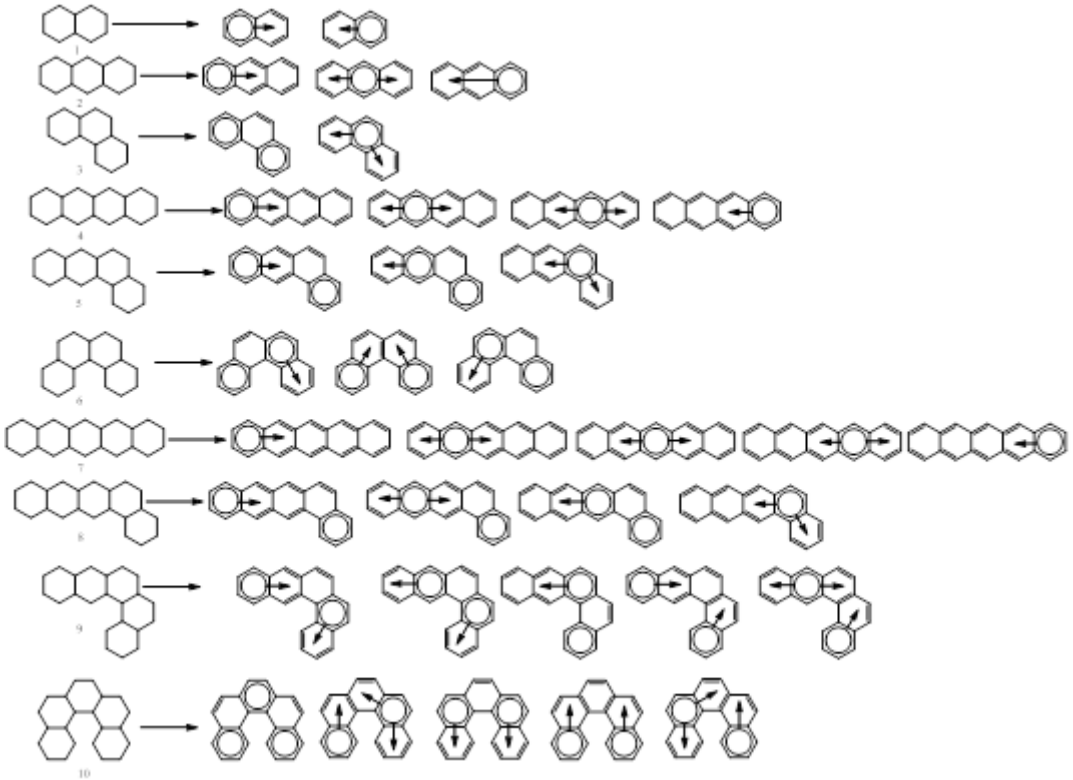


Figure 2. Representation of nine poly aromatic hydrocarbons and their Clar structures with the corresponding ring labels. Clar's aromatic π-sextets are indicated with circles

For four membered polyacenes, we can see that the average NICS values decrease when it goes to angular isomer. This fact can be explained as, in linear polyacenes, the sextet can migrate from one ring to another, i.e., the sextets are not localized in linear polyacene. Therefore, the average NICS value is much lower for **5 and 6** than for linear polyacenes **4**.

Similarly, for the hydrocarbons with five hexagons, the average NICS values for angular polyacenes are less than that of the corresponding linear one, **7**.

Table 2. The Clar 2-nomials of the selected compound and the Clar Aromaticity Index of the respective rings of the compounds.

Compound	Polynomial	CAI(α)					
		A	B	C	D	E	Average
1	$2xy$	0.71	0.71				0.71
2	$2xy + xy^2$	0.60	0.58	0.60			0.59
3	$x^2 + xy^2$	0.71	0.60	0.71			0.67
4	$2xy^2 + 2xy$	0.52	0.52	0.52	0.52		0.52
5	$2x^2y + xy^2$	0.63	0.59	0.47	0.79		0.62
6	$2x^2y + x^2y^2$	0.77	0.54	0.54	0.77		0.66
7	$3xy^2 + 2xy$	0.48	0.47	0.47	0.47	0.48	0.47
8	$x^2y^2 + 2x^2y + xy^2$	0.54	0.55	0.50	0.39	0.82	0.56
9	$x^2y^3 + 3x^2y^2 + x^2y$	0.63	0.66	0.44	0.59	0.75	0.61
10	$x^3 + 2x^2y^2 + 2x^2y^3$	0.77	0.57	0.48	0.57	0.77	0.63

The average HOMA values of individual rings are greater where the sextets are localized. The trend is nicely followed in case of hydrocarbons with ring size 5. However, the average HOMA values for four membered rings differ to some extent from this trend. In this case, the structure **6** with more sextets shows a lower HOMA value compared to that estimated for structure **5** with fewer sextets**.** This observation may be explained on the basis of the strain involved with the structures. Qualitatively, it is evident that the strain involved in the structure **6** is more due to the bent involved in the structure compared to that involved in structure **5**. Thus, the geometry of the system gets distorted, compromising its aromaticity.

A discussion on the Clar Aromaticity Index (*CAI*) and its relation to other Aromaticity Indexes are is due here. The Clar 2-nomials of all the molecules under investigation and the Clar Aromaticity Indexes of individual rings of each system are given in **Table 2**. It is evident from the given data, that in general, the average *CAI* increases from linear to bent systems. Since the average *CAI* is determined per ring unit, the aromaticity increases per ring with an increase in the extent of bending. This explains the impelling cause for a linear polyacenes to become a helical one. The advantage of using the *CAI* over other indices is that, unlike *CAI*, other indices do not give such a nice correlation between the helicity and corresponding aromaticity of the chosen molecule. All *CAI* values are calculated using Eqn. (10). Equating HOMA values in Eqn. (10) for all chosen molecules, and subsequently doing a least square analysis, one gets the following constants: C_1 = 0.58; C_2 = 0.18; C_3= 0.38. An almost linear correlation exists between the HOMA values and CAI, as shown in **Figure 3**.

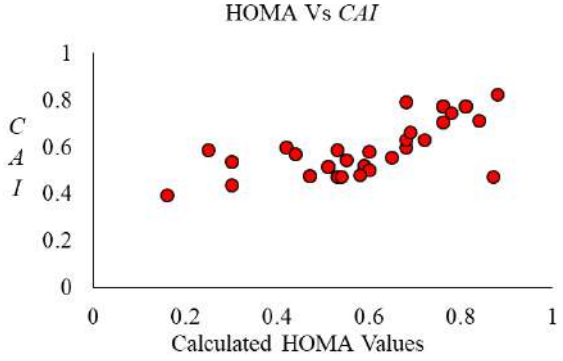


Figure 3. Comparison diagram of HOMA versus Clar Aromaticity Index values calculated using the constants as discussed in the text. The constants are derived after a least square analysis taking HOMA values into consideration.

We have also calculated the HOMO-LUMO gap ($\triangle E_{HL}$), electronegativity (***χ*)**, and hardness of the polyacenes (***η*)** (See Table 3). It has been observed that, in general, the gap is greater for the angular polyacenes than the corresponding linear polyacenes. A large $\triangle E_{HL}$ implies that the angular hydrocarbons are comparatively harder than their linear counterparts. The higher the hardness, the higher the resistance to reaction. In other words, the angular polyacenes are less reactive and have more kinetic stability. Thus, increasing helicity gives more aromatic stability as well as less reactivity. As far as electronegativity values are concerned, the electronegativity of the linear polyacenes, barring compound **6**, has a higher value than that of the angular one. Since the absolute electronegativity is a good measure of the molecular ability to attract electrons to itself, the trend in the electronegativity values of the hydrocarbons goes more or less parallel with the trend obtained from the hardness values. The exception for molecule **6** may be attributed to the strain involved in the structure, as discussed previously.

Table 3. The energy values of HOMO, LUMO, HOMO-LUMO gap ($\Delta E_{HOMO-LUMO}$), Electronegativity and Hardness of the compounds in eV unit.

Compound	E_{HOMO}	E_{LUMO}	$\Delta E_{HOMO-LUMO}$(eV)	Electronegativity (χ) (eV)	Hardness (η) (eV)
1	−0.22364	−0.04965	−4.73	3.72	4.73
2	−0.20225	−0.07197	−3.55	3.73	3.55
3	−0.22102	−0.04926	−4.67	3.68	4.67
4	−0.18858	−0.08765	−2.75	3.76	2.75
5	−0.20578	−0.06904	−3.72	3.74	3.72
6	−0.21766	−0.06289	−4.21	3.82	4.21
7	−0.17941	−0.09914	−2.18	3.79	2.18
8	−0.19252	−0.08534	−2.92	3.78	2.92
9	−0.20081	−0.07552	−3.41	3.76	3.41
10	−0.21246	−0.06107	−4.12	3.72	4.12

4. Conclusion

In this work, we have studied the aromatic character of the linear and their corresponding angular polyacenes. A total of ten molecules have been investigated. The aromaticity indexes, like Nuclear Independent Chemical Shift (NICS) values and Harmonic Oscillator Model of Aromaticity (HOMA) values, are calculated using standard software. In addition, we have establised Clar's 2-nomial for each molecule under investigation and estimated Clar Aromaticity Index (CAI) values as described by Misra et al.[22] Out of these three indexes, the Clar Aromaticity Index gives more acceptable data for the global aromatic character of conjugated hydrocarbons. It has been shown that the linear molecules are less

aromatic than the angular ones. This explains the stability of helical hydrocarbons. The other calculated parameters, like the HOMO-LUMO gap, electronegativity values, and hardness of the molecules, support the observation. However, a more quantitative measurement for a larger helical system (N-helicenes) is needed to establish the present observation on a larger farm foundation.

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CORRIGENDUM

Ricci and conformal Ricci solitons on trans-Sasakian space formswith semisymmetric metric connection

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1. The title of the paper required a modification. The modified title : *Ricci and confor- mal Ricci solitons on nearly trans-Sasakian space forms with semisymmetric metric connection*.
2. In the line 2 of 1st column of page 68 "...trans-Sasakian space form..." will be *nearly trans-Sasakian space form* and the 2nd key word "trans-Sasakian space form" will be*nearly trans-Sasakian space form*.
3. In the line 13 and line 14 of 2nd column of page 68 "...trans-Sasakian space form..." will be *nearly trans-Sasakian space form*.
4. The name of subsection 3.2 will be *Nearly trans-Sasakian space form* instead of Trans- Sasakian space form. In line 2 of subsection 3.2, "...**trans-Sasakian space form**..." will be **nearly trans-Sasakian space form**.
5. In line 7 and line 13 of 2nd column of page 70, "...trans-Sasakian space form..." will be *nearly trans-Sasakian space form*.
6. In the statement of Theorem 4.3 and Corollary 4.4 in 1st column of page 72 , "...trans-Sasakian space form..." will be *nearly trans-Sasakian space form*.
7. In the statement of Theorem 5.3 and Corollary 5.4 in 2nd column of page 73 , "...trans- Sasakian space form..." will be *nearly trans-Sasakian space form*.

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