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Preface

We would like to present, with great pleasure, the inaugural volume-9, Issue-6, June 2023, of a scholarly journal, *International Journal of Environmental & Agriculture Research*. This journal is part of the AD Publications series *in the field of Environmental & Agriculture Research Development*, and is devoted to the gamut of Environmental & Agriculture issues, from theoretical aspects to application-dependent studies and the validation of emerging technologies.

This journal was envisioned and founded to represent the growing needs of Environmental & Agriculture as an emerging and increasingly vital field, now widely recognized as an integral part of scientific and technical investigations. Its mission is to become a voice of the Environmental & Agriculture community, addressing researchers and practitioners in below areas.

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Environmental science and regulation, Ecotoxicology, Environmental health issues, Atmosphere and climate, Terrestric ecosystems, Aquatic ecosystems, Energy and environment, Marine research, Biodiversity, Pharmaceuticals in the environment, Genetically modified organisms, Biotechnology, Risk assessment, Environment society, Agricultural engineering, Animal science, Agronomy, including plant science, theoretical production ecology, horticulture, plant, breeding, plant fertilization, soil science and all field related to Environmental Research.

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Each article in this issue provides an example of a concrete industrial application or a case study of the presented methodology to amplify the impact of the contribution. We are very thankful to everybody within that community who supported the idea of creating a new Research with *IJOEAR*. We are certain that this issue will be followed by many others, reporting new developments in the Environment and Agriculture Research Science field. This issue would not have been possible without the great support of the Reviewer, Editorial Board members and also with our Advisory Board Members, and we would like to express our sincere thanks to all of them. We would also like to express our gratitude to the editorial staff of AD Publications, who supported us at every stage of the project. It is our hope that this fine collection of articles will be a valuable resource for *IJOEAR* readers and will stimulate further research into the vibrant area of Environmental & Agriculture Research.

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Rainfall Anomaly Index over Mouhoun Basin in Southwestern Burkina Faso

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Abstract**—** *In recent decades, climate index has become an important tool in hydrological studies. Accordingly, the implication of climate change in hydrological researches requires the assessment of historical and future climate characteristics to understand current and future processes for water resources management improvement. The aim of this study is to analyze historical rainfall anomalies over the Mouhoun watershed by applying precintcon package in R studio. Required data for the assessment of the rainfall anomalies was retrieved from the National Meteorological Agency (NMA) of Burkina Faso. Purposely, monthly rainfall data of three meteorological stations spanning from 1980 to 2012 were collected. The findings revealed that within Mouhoun watershed, the rainfall data are leptokurtic and the distribution is narrower than normal. This result shows thus a moderate dry rainfall anomaly. During the second period of analysis (1990-1994), The station of Bobo Dioulasso is showing an estimated value of -2.594. This value of the RAI is indicating a slightly dry pattern of rainfall in this station. However, the stations of Boromo, is presenting a value of RAI in the range of -1. 00 to -1.99 highlighting a moderate dry rainfall characteristic. During the period (1995-1999), slightly dry conditions are detected in Bobo and Boromo. From 2000 to 2004 and 2005 to 2011, moderate dry RAI index is identified for all station except for the station of Gaoua. Among these six stations of the watershed, Gaoua station which is located in the southwestern part of the watershed has experienced throughout the period of analysis a dryness conditions. Indeed, a slightly dry rainfall anomaly is detected with a RAI ranging from -0.50 to -0.99. The results obtained could serve as a guide to decision makers in water and climatic management.*

Keywords**— *Rainfall, variability, climatic change, meteorological drought.***

I. INTRODUCTION

Rainfall as one of the main components of the hydrological cycle (Shiklomanov et al. 2000; Schneider et al.; 2010; Li et al.,2022b) is undergoing changes worldwide. Indeed, global warming is substantially leading to potential change in rainfall occurrence all over the world. As reported by IPCC (2022), an increase of temperature up to degree, may results in huge rainfall variability. Consequently, climate change, is greatly affecting the patterns of rainfall. The Sahel region, highly exposed to climate change, is gradually becoming hotter, with some areas experiencing increased and erratic rainfall. Historical records and climate projections show that the magnitude and frequency of precipitation extremes are increasing in Sahelian areas considering global, regional, and local scales. According to Nicholson et al, (2018) significant rainfall fluctuations has been registered in the Sahel. Indeed, over the last few decades, rainfall in this region has experienced profound changes such as drought and flood. Moreover, Martin et al (2016) revealed that high variabilities sound to occur in the next coming decades leading to an inappropriate water resources management. Consequently, analyzing rainfall records stand to be an important step in water resources management (Kim et al 2012; Dastorani, 2016; Borah et al; 2021). Several studies have investigated temporal and spatial changes in rainfall within Burkina Faso. Various rainfall-based indices were used to investigate the rainfall variability conditions in Burkina Faso. Using Standardized Anomaly Index (SAI), Kima et al (2015) found an upward trend, with high inter-annual variability in the Boulgou' province of Burkina Faso. While, Sagnan et al (2021) applied a standardized precipitation index to analyze the water balance in Burkina Faso. They found a slight increase in rainfall over the country in the 1990s. Over the recent years, Rainfall anomaly index analysis has become more popular in recent years (Costat 2017, Raziei 2021). Hänsel et al. (2016) applied the Modified Rainfall Anomaly Index (mRAI) in evaluating its suitability as an alternative to the Standardized Precipitation Index (SPI) in assessing future precipitation conditions. Applying Standardized precipitation evapotranspiration index (SPEI) and standardized precipitation index (SPI) to classify the precipitation and water balance anomalies in four deleted Sub-Saharan Countries (Senegal, Burkina Faso, Tanzania, and Malawi.), Mbaye et al. 2022 found high rainfall variability of extreme events in all the four countries. In a recent study, Aryal et al. (2022) applied the RAI to characterize the droughts in Népal and to evaluate their impacts on crop yields. Although rainfall analyses in Mouhoun watershed have been done by many methods such as SPI and, rainfall anomaly index analysis within the basin is still lacking. However, a number of studies have shown a comparable performance of RAI to the SPI (Keyantash and Dracup 2002; Loukas et al. 2003). According to Keyantash and Dracup (2002), the RAI offers a higher degree of transparency and tractability and demands a lower degree of sophistication than the SPI with regard to the evaluation criteria for drought indices. Analyzing the comparative performance of three meteorological drought indices, Oladipo (1985) found that differences between the RAI and the more complicated indices were negligible. Moreover, the results of the analysis suggest that precipitation is the most important climatic element as an input into meteorological drought. Therefore, the present study estimates the value of RAI within the Mouhoun watershed in order to provide robust evidence on historical rainfall characteristics for decision making.

II. RESEARCH METHODOLOGY

2.1 Description of the study area

The Mouhoun River basin is located in western Burkina Faso and spans from 5°-2° W to 9°-14° North. The watershed covers an area of 91 036 km² that account of 22.32% of the Volta River basin. This transboundary River extends on 1000 km in Burkina Faso and is divided into three national sub-basins: the upper Mouhoun (20 978 km^2) and the Lower Mouhoun (54 802 km^2) and the Sourou (15 225 km^2). The upper Mouhoun has perennial flows in its upstream part with low water levels that are rarely less than 2 m^3/s both at the Samandéni station and on the Kou at Nasso. The Upper Mouhoun limited to the confluence of the Sourou is mainly drained by five main tributaries which are the Plandi, the Kou, the Voun Hou. In general, during floods the Mouhoun drains its tributaries but during recession, a reverse situation is observed since it is the Sourou that drains the Mouhoun. The lower Mouhoun abruptly changes direction after the loop of the Sourou, it flows towards the south-east, then due south, forming the border with Ghana from Ouessa. The part of the Mouhoun river under study crosses the Sudano-Guinean and Sudanese climatic zones, with average annual rainfall between 750 and 1050 mm. The relief of the basin is quite monotonous with an average slope of 2%. The altitudes are between 273 m and 733 m (Tiemtore, 2017) The vegetation cover of the basin is essentially made up of wooded savannas, open forests and forest galleries along the permanent watercourses, whose width increases as one goes southward. Due to its geographical location, the study area enjoys a Sudanese type climate with an average annual rainfall of over 900 mm. Over the last fifty years, there has been a decline in annual rainfall in the 1970s and 1980s and an increasing trend over the last two decades (figure 6)

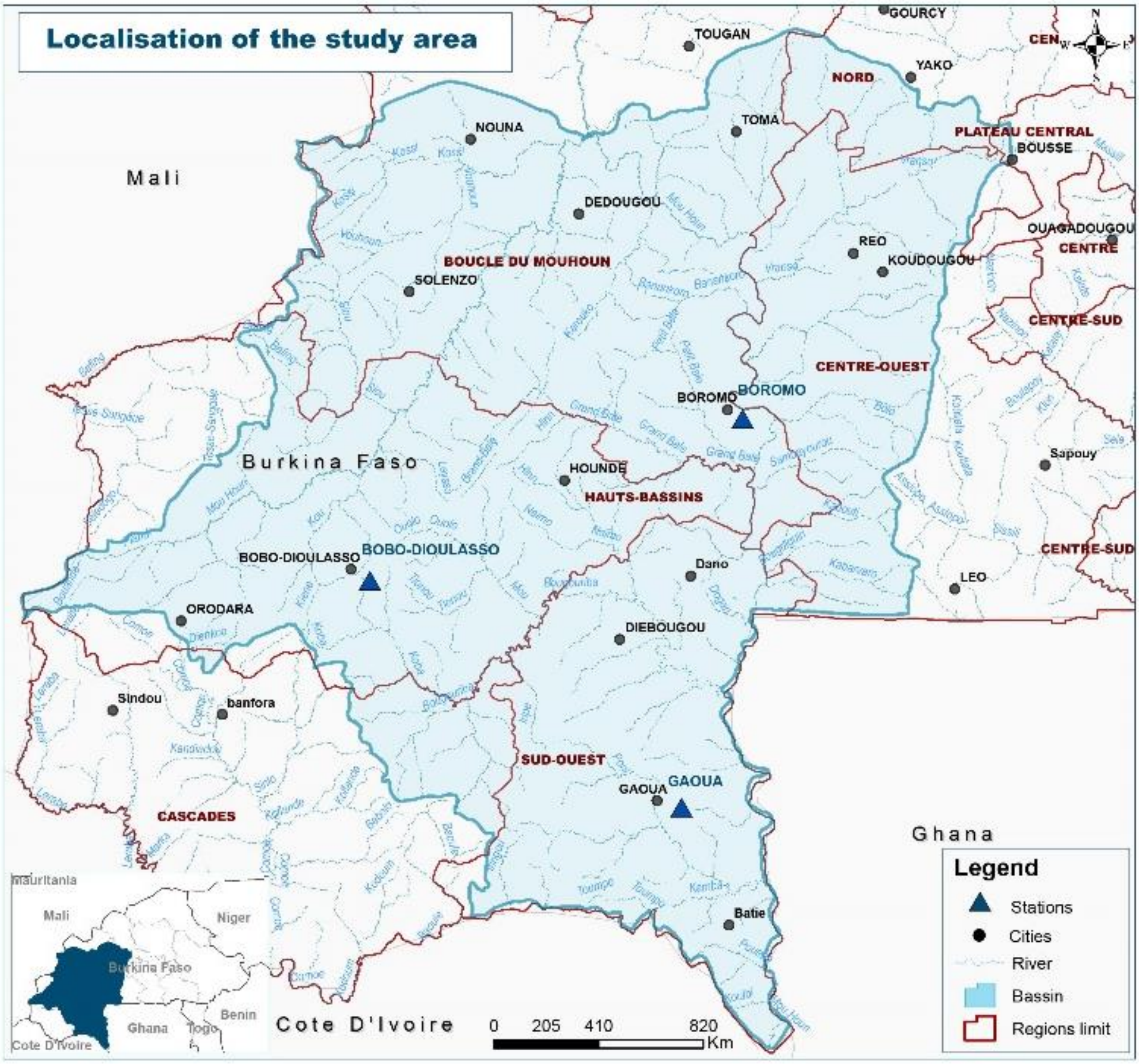

FIGURE 1: Localization of the study area

2.2 Data

Monthly rainfall data from 1980 to 2012 were provided by the National Meteorological Service (DGM) of Burkina Faso. Three rainfall stations, spread across, the Mouhoun catchment were selected (Fig. 1). Missing value were completed using regression method.

2.3 Assessment of Normality

To test the normality of the dataset, the skewness and the kurtosis of the data was estimated. Then, the Shapiro test was performed for all stations. As stated by Kim et al (2013), Skewness is a measure of the asymmetry of a variable and kurtosis is a measure of 'peakedness' of a distribution. The skew value of a normal distribution is zero, usually implying symmetric distribution. According to West et al. (1996) a positive skew value indicates that the tail on the right side of the distribution is longer than the left side and the bulk of the values lie to the left of the mean. Controversially, a negative skew value indicates that the tail on the left side of the distribution is longer than the right side and the bulk of the values lie to the right of the mean.

The following equation shows the formula of the skewness. The test is based on the density function, which is divided into slices through class intervals. The smaller the value of the chi-squared statistic, the better the expected fit of the model to the sample at hand, which is computed by:

$$\boldsymbol{S_k = \frac{\frac{\sum_{i=1}^{N}(k_i - \bar{k})^3}{N}}{\sigma_{\bar{k}}{}^3}} \tag{1}$$

Similarly, the Kutosis test allow to detect the normality of the data set. The Kurtosis is defined as the ratio of the mean square successive difference between the years to the variance. The test statistic is given as follow:

$$\boldsymbol{K_u = \frac{\frac{\sum_{i=1}^{N}(k_i - \bar{k})^4}{N}}{\sigma_{\bar{k}}{}^4}} \tag{2}$$

The Shapiro-Wilk test which was introduced by Shapiro et al (1965) is a normality test designed to detect all departures from normality. The estimations for this test are based on the algorithm developped by Royston (1995). Indeed, the Shapiro-Wilk test relies on a correlation of sample “order statistics” with statistics of a normal distribution. The Shapiro-Wilk test statistic W is defined as:

$$W = \frac{\left(\sum_{i=1}^{n} a_i X_{(i)}\right)^2}{\left(\sum_{i=1}^{n}(X_{(i)} - \bar{X}\right)^2} \tag{3}$$

Where $X_{(1)} \leq X_{(2)} \leq \ldots\ldots \leq X_{(n)}$ are the ordered values of the sample and a_i are tabulated constants. Normality is rejected for small values of W.

2.4 Estimation of the Rainfall Anomaly Index (RAI)

The rainfall anomaly index (RAI), designed by van Rooy in 1965, is used to identify positive and negative precipitation anomalies over a historical series. According to Rooy (1965), the RAI aims to make the comparison between precipitation deviations in different regions feasible. The first step in applying RAI is to rank in descending order of magnitude the precipitation values for the period of study. Then, the mean of the ten highest precipitation values and the mean of the ten lowest precipitation values for the period of study are estimated. The positive and negative RAI indices are computed by using the mean of ten extremes.

The RAI is expressed as follows:

$$RAI = 3\left[\frac{N - \bar{N}}{\bar{M} - \bar{N}}\right] \textit{for the positive anomaly} \tag{4}$$

$$RAI = -3\left[\frac{N - \bar{N}}{\bar{X} - \bar{N}}\right] \textit{for the negative anomaly} \tag{5}$$

where N is the current monthly/seasonal/annual precipitation;

$\bar{N}$ stands for the average monthly precipitation of the dataset

$\bar{M}$ represents the average of ten highest monthly precipitations record

$\bar{X}$ is the average of ten lowest monthly precipitations record;

$N - \bar{N}$ refers to the positive anomaly and negative anomaly based on positive or negative values.

The classification of the index used by Rooy (1965) is as follows.

TABLE 1
THE CLASSIFICATION OF THE INDEX USED BY ROOY (1965)

S /n	RAI	Class Description	S /n	RAI	Class Description
1	**≥3.00**	**Extremely wet**	6	**-0.50 to -0.99**	**Slightly dry**
2	**2.00 to 2.99**	**Very wet**	7	**-1.00 to -1.99**	**Moderate dry**
3	**1.00 to 1.99**	**Moderate wet**	8	**-2.00 to -2.99**	**Very dry**
4	**0.50 to 0.99**	**Slightly wet**	9	**≤-3.00**	**Extremely dry**
5	**0.49 to -0.49**	**Near Normal**			

III. RESULTS AND DISCUSSION

3.1 Normality assessment

The Normality test results presented in Table 2 indicate that the rainfall records are significantly skewed to the right (Skewness = 1.264701, 1.396572, and 1.277155 respectively in Bobo Dioulasso, Boromo and Gaoua stations). As stated in Hennessy (2009), a normal distribution exhibits zero skewness, while negative values indicate that the distribution has a heavy left tail and positive values indicate that the distribution has a heavy right tail. Based on the results obtained from the three stations, it can be concluded that across Mouhoun watershed, the rainfall distribution has a heavy right. In addition, table 1 also presents estimates kurtosis for each station. There are three categories of kurtosis that a set of data can display. When kurtosis is equal to 3, the distribution is mesokurtic; a kurtosis of less than 3 indicates that the distribution is broader than normal and is termed platykurtic; while a kurtosis of greater than 3 is characterized as leptokurtic and the distribution is narrower than normal. The results show that in all station the value of the Kurtosis is greater than 3 meaning that the data are leptokurtic and the distribution is narrower than normal. As far as the Shapiro test is concerned, the test rejects the hypothesis of normality when the p-value is less than or equal to 0.05. In all stations, the p-value of the Shapiro test turns out to be less than 0.05. Consequently, the sample data comes from a population that is normally distributed. Then, the null hypothesis that the data are normally distributed is rejected.

TABLE 2
NORMALITY TEST OF THE DATA SET

Station	*Skewness*	*Kurtosis*	*Shapiro test*	
			W	**p-value**
BOBO	1.264701	3.929249	0.82233	3.647e-16
BOROMO	1.396572	4.681616	0.80562	2.2e-16
GAOUA	1.277155	5.493497	0.86978	6.678e-14

3.2 Identification of rainfall anomaly in the Mouhoun watershed

Based on the classification of the RAI (Table 1), all the stations are presenting a negative value of RAI (Table 3). From 1985 to 1989, a value of -1,13 is registered at Bobo Dioulasso station, -1,17 is identified at Boromo station while the station of Gaoua is indicating -0,82 as the value of the RAI. This result shows thus a moderate dry rainfall anomaly. During the second period of analysis (1990-1994), the stations are showing an estimated values of -0,95 and -0,88, respectively in Bobo Dioulasso and Gaoua. These values of the RAI are spanning from -0.50 to -0.99 indicating a slightly dry pattern of rainfall. However, the station of Boromo is presenting a value of RAI in the range of -1.00 to -1.99 highlighting a moderate dry rainfall characteristic. During the period (1995-1999), slightly dry conditions are detected in Bobo, Boromo and Gaoua. From 2000 to 2004 and 2005 to 2011, moderate dry RAI index is identified for all station except for the station of Gaoua which is showing a slightly dry condition with a value of RAI being -0,75. Among these six stations of the watershed, Gaoua station which is located in the southwestern part of the watershed has experienced throughout the period of analysis a dryness conditions. Regardless of the time period, the overall results indicate slightly to moderate dry rainfall anomaly and this situation may lead to drought, severe shortages, low productivity, migration. Regarding the high important role given to water resource, the availability of this resources during different parts of the year are of key importance for an agricultural country like Burkina Faso specifically (Yabre et al., 2023). Indeed, the Mouhoun basin is the most fertile area of Burkina Faso and is considered as the granary of the country (Gray, 1999; McCorkle, 2019; Ouedraogo, 2022). In addition, as stated by Vlavonou et al (2020), the Boucle du Mouhoun, Center-West and South-West regions are predominantly agricultural and nearly 50% of their GDP is generated by the agricultural sector. However, high variability of rainfall affects crops production potentialities. Therefore, the assessment of the Rainfall Anomaly index in a region are that significant for reducing its vulnerability to the negative impacts of drought.

TABLE 3
VALUES OF THE RAINFALL ANOMALY INDEX WITHIN MOUHOUN WATERSHED

	1985-1989	1990-1994	1995-1999	2000-2004	2005-2011	MEAN
BOBO DIOULASSO	-1,13	-0,95	-0,86	-1,03	-1,13	-0,9925
BOROMO	-1,17	-1,13	-0,95	-1,20	-1,07	-1,0875
GAOUA	-0,82	-0,88	-0,65	-0,72	-0,75	-0,75

IV. CONCLUSION

In this paper, the Rainfall Anomaly index was performed on rainfall data recorded within Mouhoun watershed during 1985–2011. It comes out this study that drought characteristics within Mouhoun watershed is not significant. Indeed, moderate to slightly dry rainfall anomaly is identified across the basin. A slightly dry trend is observed in Bobo Dioulasso and Gaoua during the period of analysis while the station of Boromo showed a moderate trend. The findings may provide some basic rainfall characteristic for other scholars in this basin. In addition, this may help in water resources planning for decision making.

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Vermicomposting: A Solution to Noxious Emissions in the South Asian Subcontinent

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Abstract— *One of the most significant threats to the environment is posed by the ever-increasing generation of waste. This has resulted in an urgent need for global waste management techniques that integrate the ideas of recycling and reusing of the essential components of waste. The current technologies of waste management including incineration, landfills, and material recovery have not proven as useful as intended. These mostly outdated methods have resulted in generation of toxic fumes, health hazards, and high energy and operation costs. Thus, a unique, safe, hygienic, and sustainable method of waste management is essential.*

Vermicomposting is a low-cost, eco-biotechnological process of waste treatment in which earthworms are used to biodegrade the organic waste into useful nutrient-rich vermicast. The products of this waste treatment process are disinfected, detoxified and nutrient-rich bio-organic fertilizers. The process not only recycles organic wastes, but also helps improve soil structure and contents. This review provides an insight into the design, operation, commercialization, and factors affecting the vermicompost reactors.

Keywords— Biofertilizers, crop-burning, Emissions, Rice husk, Vermicomposting.

I. INTRODUCTION

According to the UN World Population Prospects, it is predicted that the world population will reach 9.74 billion by 2050. (United Nations, 2019) The ever-increasing human population has resulted in a significant increase in global waste generation and pollution. Approximately 1300 million tons (MT) of solid waste is generated annually in the major cities of the world, an amount projected to rise to 2200 MT by 2025. (Hoornweg & Bhada-Tata, 2012) Solid waste generation is positively related to the level of income and urbanization. On an average, developing countries including India, Pakistan, and Bangladesh, generate over 0.70 kg of solid waste per individual per day. (Troschinetz et al, 2009) It is estimated that 1.8 MT of solid waste per day will be generated in Asia alone by 2025. (Dasgupta, 2014; Yoshizawa et al., 2004) Table 1 compares the waste generation in Asia during the year 1995 and 2025 (projected values) (Hoornweg, 1999).

Waste disposal is a pressing issue, as the existence of widely spread waste imperils the environment in general and soil health in particular. The rapid development of human society creates imbalances in nature through rapid urbanization, industrialization, and infrastructure development, all of which cause deterioration of soil health. As the overall environmental milieu is polluted, humans are also affected.

When disposing waste, system complexities and the integrated nature of materials and pollution are quickly apparent. For example, waste incineration is expensive and poses challenges of air pollution and ash disposal. Incineration requires waste placed outside for collection to be containerized to stay dry, and much of the waste stream is not combustible. Landfills require land availability, and siting is often opposed by potential neighboring residents. Solving one problem often introduces a new one, and if not well executed, the new problem is often of greater cost and complexity. Most approaches to waste disposal lead to soil deterioration, toxic effects, and increased pollution of the land, air, and water and have an adverse impact on living beings in addition to the expense involved. To address this issue, we need an eco-friendly, one-step solution for managing wastes that also provides a beneficial end-product.

TABLE 1
1995 AND 2025 MUNICIPAL SOLID WASTE GENERATION IN ASIA[4]

	GNP per Capita (USS)		**Urban Population (% of Total)**		**MSW generation (kg day^{-1} per capita)**	
Country	1995	2025	1995	2025	1995	2025
Low Income	490	1050	27.8	48.8	0.64	0.6-1.0
Nepal	200	360	13.7	34.3	0.5	0.6
Bangladesh	240	440	18.3	34.3	0.49	0.6
Myanmar	240	580	26.2	47.3	0.45	0.6
Vietnam	240	580	20.8	39	0.55	0.7
Mongolia	310	560	60.9	76.5	0.6	0.9
India	340	620	26.8	45.2	0.46	0.7
Laos	350	850	21.7	44.5	0.69	0.8
China	620	1500	30.3	54.5	0.79	0.9
Sri Lanka	700	1300	22.4	42.6	0.89	1
Middle Income	1410	3390	37.6	61.1	0.73	0/8-1.5
Indonesia	980	2400	35.4	60.7	0.76	1
Philippines	1050	2500	54.2	74.3	0.52	0.8
Thailand	2740	6650	20	39.1	1.1	1.5
Malaysia	3890	9400	53.7	72.7	0.81	1.4
High income	30990	41140	79.5	88.2	1.64	1.1-4.5
Republic of Korea	9700	17600	81.3	93.7	1.59	1.4
Hong Kong	22990	31000	95	97.3	5.07	4.5
Singapore	26730	36000	100	100	1.1	1.1
Japan	39640	53500	77.6	84.9	1.47	1.3

Widely regarded safe and sustainable strategies to treat organic wastes include best-known practices of composting and vermicomposting for biological stabilization of solid organic wastes by transforming them into a safer and more stabilized material that can be used as a source of nutrients and soil conditioner in agricultural applications (Lazcano et al, 2008; Bernal et al, 2009). Vermicomposting is one of the most efficient means to mitigate and manage environmental pollution problems. It is the process in which earthworms are used to convert organic materials (usually wastes) into a humus-like material known as vermicompost. The goal is to process the material as quickly and efficiently as possible.

II. VERMICOMPOSTING: BASIC PROCESS

Vermicomposting is defined as a bio-oxidative process in which earthworms interact with microorganisms and other fauna within the decomposer community, accelerating the stabilization of organic matter and greatly modifying its physical and biochemical properties. (Gomez-Brandon et al, 2014) Vermicomposting is a bio-conversion process whereby organic waste is turned into vermicasts by the action of epigeic earthworms (Jadia et al 2008). The earthworms eat up the organic waste (feed) and expel it as vermicasts (product), which are dark brown solid particles in nature (M. M. Manyuchi, 2012). These vermicasts are rich in the primary nutrients of a fertilizer i.e. nitrogen (N), phosphorous (P) and potassium (K) (Jadia et al 2008; M. M. Manyuchi et al. 2012; A. A. Ansari et al. 2010). Furthermore, a leachate called vermiwash is produced alongside the vermicasts and is also rich in NPK (M. Gopal et al. 2010; V. Palanichamy et al. 2011; C. Sundaravadivelan et al. 2011; G. Nath et al. 2012).

Vermicomposting has a unique position in environmental and chemical engineering as it is the only pollution control process that uses multicellular animal as a bioagent. (Abbasi et al 2009) It is a process of stabilization of organic material through the joint action of earthworms and micro-organisms. Microbes are responsible for the biochemical degradation of organic matter, while earthworms are important drivers to condition the substrate and alter the biological activity. (Suthar 2009) This joint action of earthworms and microbes results in a higher-quality end product compared to conventional composting process.

Vermicomposting is carried out in different vermireactors such as the windrows, bins, and flow-through systems (G. Munroe, Year unknown). Vermireactors are biological reactors where earthworms' activities take place. Windrows and bins are batch vermireactors whereby the earthworms, bedding and feed are put initially and the vermicomposting process is allowed to take place until all the vermicasts are obtained at a given retention time (G. Munroe, Year unknown).

III. ROLE OF EARTHWORM IN VERMICOMPOSTING

Earthworms are invertebrates belonging to the phylum Annelida, class Oligochaeta and family Lumbricidae. The earthworms are long, elongated, cylindrical, soft bodied animals with uniform ring like structures consisting of segments along the length of their body outwardly highlighted by circular grooves. There are about 3320 species of earthworms all over the world (Bhatnagar et al 1996), but hardly 8–10 species are suitable for vermicompost preparation. Earthworms have been extensively utilized for the recycling of a variety of organic wastes like municipal solid wastes (Ciavatta et al 1993) wheat straw, sewage sludge, forestry waste, vegetable waste (Vallini et al. 1989), farmyard manure etc. Epigeic (Greek word "upon the earth") worms live on the surface litter and feed on decaying organic matter. They do not have any permanent burrows and are the type of worm widely used in vermicomposting.

Earthworms act as grinder, crusher, chemical degrader, and a biological stimulator of waste material. (Binet et al 1998) Earthworm hosts millions of biodegrading microbes, hydrolytic enzymes and hormones that help in rapid decomposition of complex organic matter into vermicompost in a relatively smaller duration of time. The mechanism of formation of vermicompost by earthworms occurs in following steps; organic material consumed by earthworm is softened by the saliva in the mouth of the earthworms. Food in esophagus is further softened and neutralized by calcium resulting in particles of size less than < 2µm, thereby giving an enhanced surface area for microbial processing. This finally ground material is exposed to various enzymes such as protease, amylase, lipase, cellulase and chitinase secreted in lumen by stomach and small intestine (Dominguez et al 2010). Moreover, microbes associated with intestine facilitate breaking down of complex biomolecules into simple compounds. Only 5–10% of the ingested material is absorbed into the tissues of worms for its growth and the rest is excreted as vermicast. The vermicast is a good organic fertilizer and soil conditioner. High-quality vermicast can be produced by worms such as the red wrigglers (E. fetida) as it contains humus with high levels of nutrients that has good potential to produce organic fertilizer. Figure 1 gives a detailed breakdown of the role of each part of an earthworm in the vermicompost production process. (Lemtiri et al. (2014).

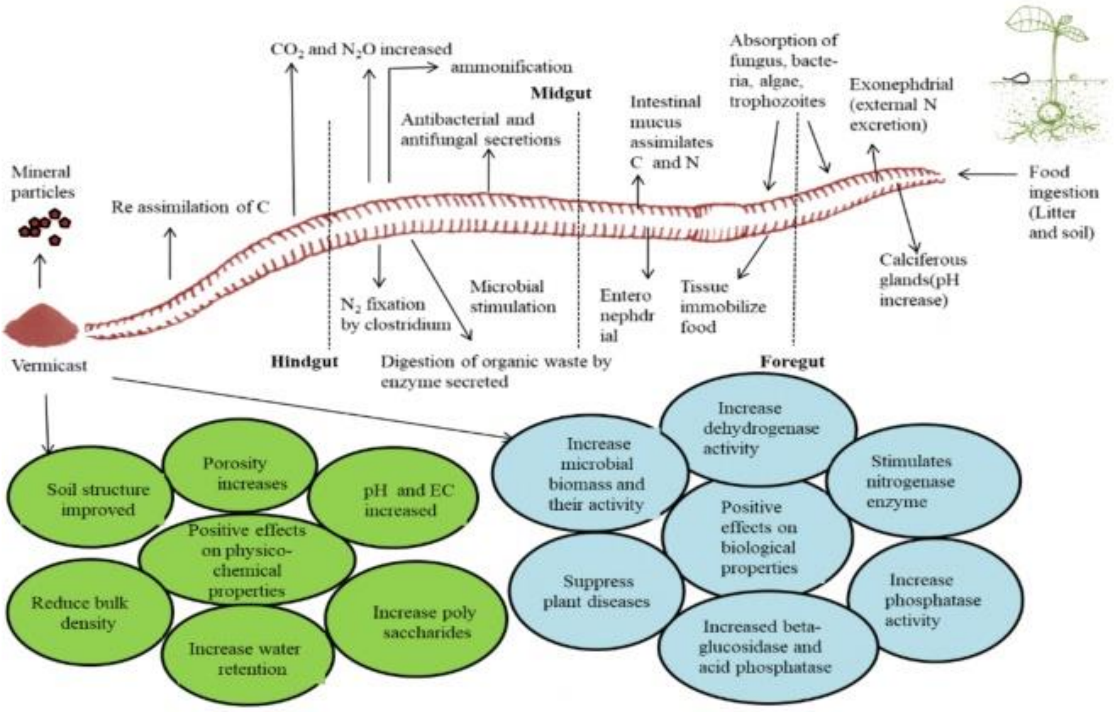


FIGURE 1: Process of vermicomposting in an earthworm and its consequences (Lemtiri et al. (2014)

IV. REACTOR DESIGN

The vermicomposting process is designed to ensure optimum processing of the organic waste. The organic waste is first shredded to reduce the particle size. The organic waste is then pre-composted for a short period of time usually a week while the pH and moisture content in the feed is monitored. Earthworms function well in a pH range of 5.0-9.0, temperatures below 45°C and moisture content of 45-75% (M. M. Manyuchi, 2012). Pre-composting facilitates in making available the other organisms that can aid the vermicompost process and by reducing the organic waste surface area the earthworms will act on. The feed is then introduced into a flow-through vermireactor whereby the vermicomposting process is initiated by adding the earthworms. pH, temperature, and moisture content are continually monitored whilst the vermicasts and vermiwash produced are collected at the bottom of the vermireactor for storage. Figure 2 shows a process flow diagram for a simple flow-through vermicompost production.

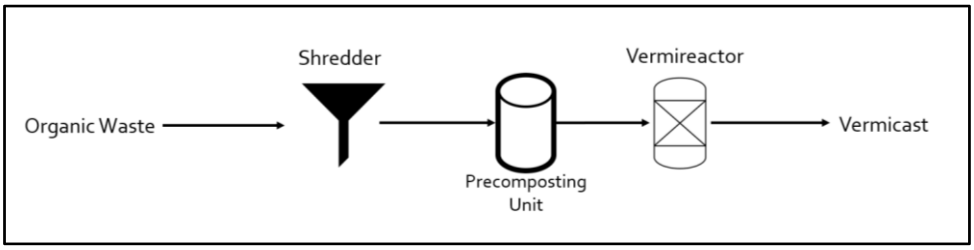


FIGURE 2: Process flow diagram showing each component of vermicomposting.

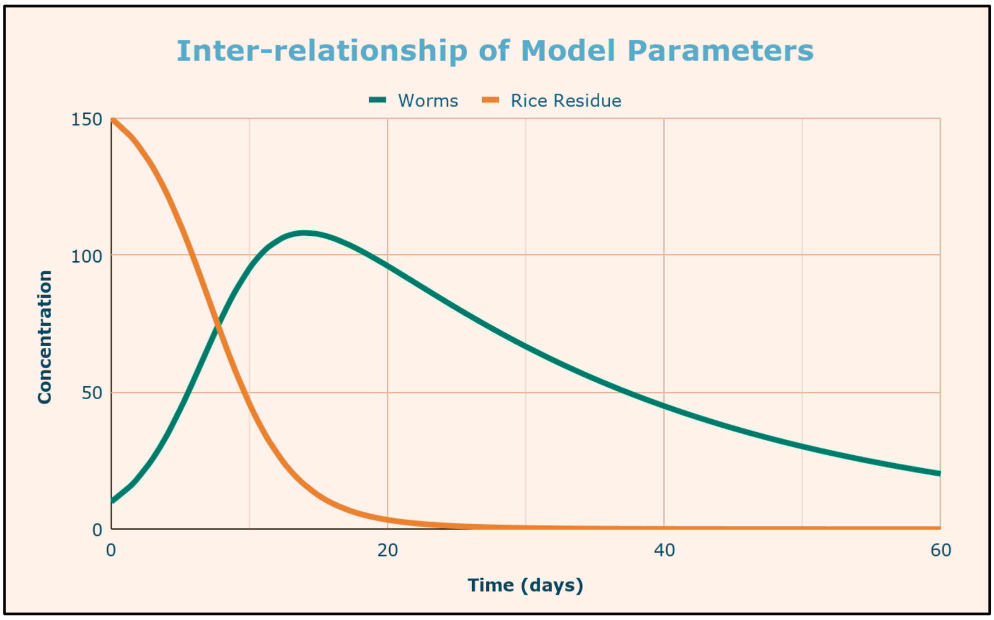
The vermicomposting process has certain parameters that need to be considered in deriving a simple kinetic model. The vermireactor can be seen as a system consisting of two main parameters which are Earthworms and organic wastes (for purpose of this example we will be considering rice residue as the organic wastes). Using these parameters, a model can be proposed for their inter-relationship.

Once the two components of the reaction are mixed, the earthworms will use the rice residue to metabolize and increase in population, shown in Equation 1. After a certain time, when there is no more rice residue to be bio-degraded, there will be an unavailability of sufficient nutrients in the system and the earthworms will eventually die off, as shown in Equation 2.

Worms + Rice Residue → 2 Worms

Worms → Death of Worms

To further analyze the inter-relationship of the parameters present in the system, a graph can be generated to visually see the relationship. As shown in the graph below, as the Rice Residue concentrations decrease exponentially, the earthworm concentration present increases exponentially. Once the rice residue concentration tapers off and reaches approximately zero within 25 days, the earthworm concentration begins to decrease over the time. It is imperative to note that the earthworm concentration is assumed to be one-tenth (1/10) of the concentration of rice residue at the start.



GRAPH 1: Inter-relationship of the Model Parameters.

Although vermicomposting approximates as a continuously stirred tank reactor (CSTR) in which the contents are mixed and aerated, the reactor is unique in design and operation. The earthworms in the vermireactors function as 'reactors within reactors' in the sense that the entire processing of the substrate from the reactant to the product occurs within each worm. Thus, an integral part of the reactor design is to understand and model the earthworms as a separate reactor units inside the vermireactor. (Abbasi et al 2008)

The digestive tract of the earthworm extends the whole length of its body as a long tube, which starts from the mouth and ends at the anus (Edwards and Bohlen 1996). The tubular gut of earthworm is assumed to be a plug flow reactor (PFR) possessing an input and output (Figure 3). The entering food particles via mouth move at a constant rate (steady state) with perfect radial mixing and the digestion proceeds according to first-order kinetics (Levenspiel 1999).

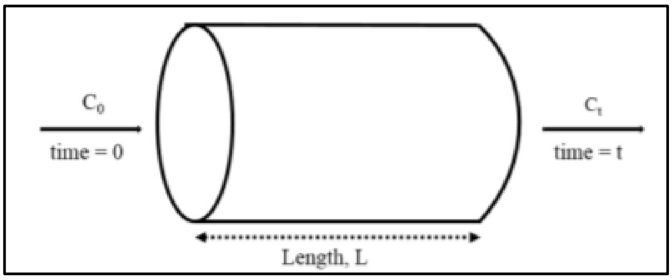


FIGURE 3: Diagrammatic representation of a plug-flow reactor showing an input and output

Considering each earthworm as a PFR, we can express the first order kinetics based on the following general-mass balance equation,

Accumulation = Input − Output + Generation – Consumption

The general equation expressing rate (r) at which mass or volume of a material C changes with time along the gut of earthworm can be given as below:

$$\textbf{Rate} = \frac{dC}{dt} = -\textbf{kt}$$

where C is the concentration of the reacting substance, per unit time t and k is the first-order rate constant. This general equation can be integrated within the limits of concentration C_0 and C_t at the time t=0 and t, respectively, to give:

$$\int_{C0}^{Ct} \frac{dC}{C} = -k \int_{0}^{t} dt$$

Upon integration,

$$\ln[C]t - \ln[C]0 = -k\,t$$

From the laws of algorithm, equation 3:

$$\ln\frac{[C]0}{[C]t} = -k\,t$$

The linear pattern of digestion kinetics observed by Kiyasudeen et. al 2018 (figure 4) provides ample evidence that the earthworm gut can be modeled as a PFR. The kinetic result demonstrated that the gut sections expressed a linear pattern of digestion, thus, supporting PFR behavior. However, an evident deviation in the foregut region was also identified. The deviation could be due to the activity of digestive organs such as gizzard and crop in the pre-intestine region, which are known to enhance the surface area for the microbes apart from their role of enzymatic secretions (Hickman 2005).

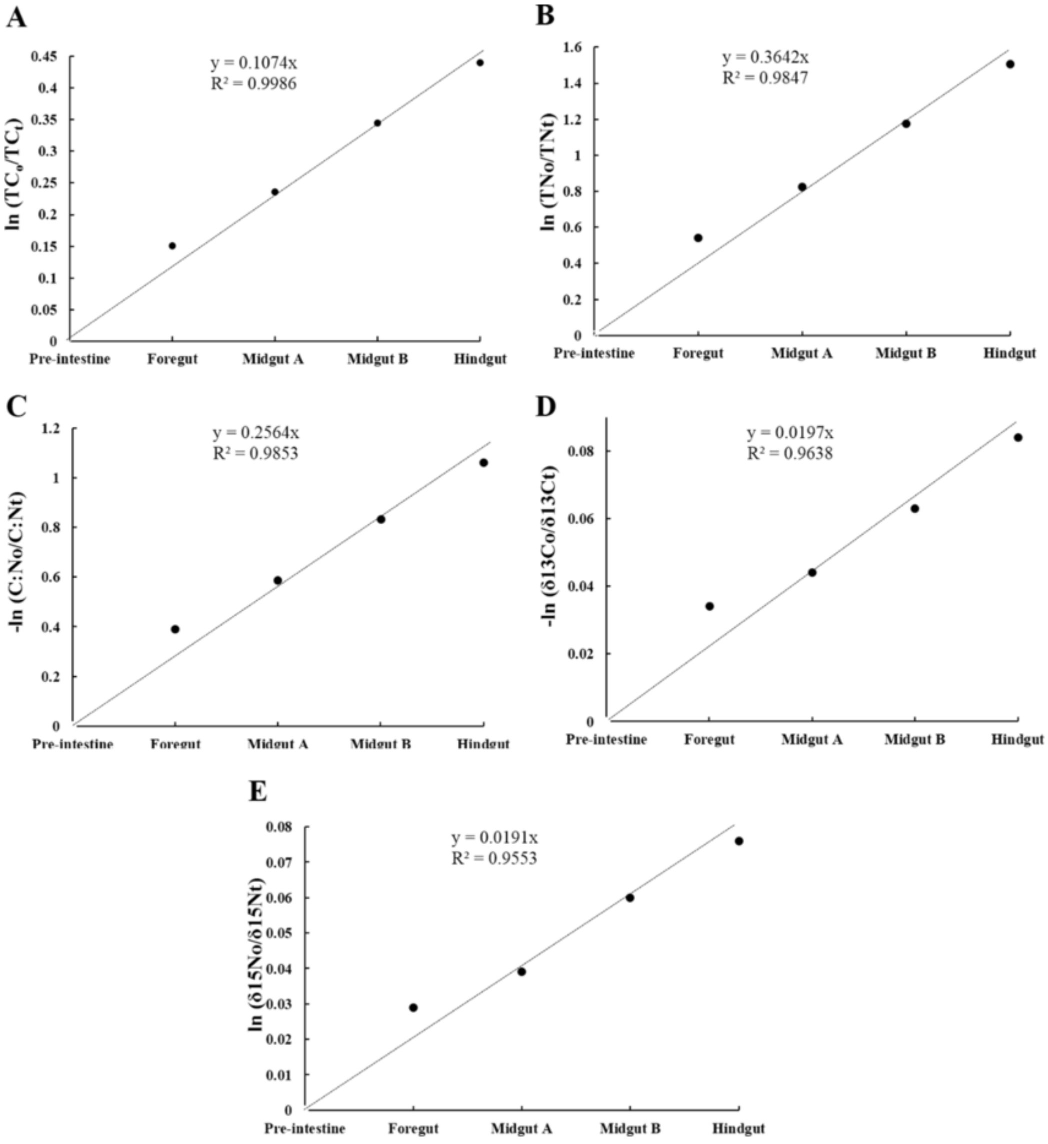


FIGURE 4: Digestion kinetics (first-order) of total carbon (a), total nitrogen (b), C/N (c), δC^{13} (d), and δN^{15} (e) during gut transit in earthworms calculated using equation 3.

V. FACTORS AFFECTING VERMICOMPOSTING

The most important factors which affect vermicomposting process include moisture, pH, temperature, aeration, pH value, ammonia and salt content.

5.1 Moisture

A strong relationship exists between the moisture content of organic wastes and the growth rate of earthworms. A study on vermicomposting process and earthworm's growth at different temperature and moisture ranges showed that 65–75% is most suitable range of moisture at all ranges of vermicomposting temperature (Suthar S. 2007). The bedding material for vermicomposting must be able to hold enough moisture as earthworms respire through their skins and moisture content less than of 45% can be fatal to the worms.

Although epigenic species, E. fetida and E. andrei can survive moisture ranges between 50% and 90%, they grow most rapidly between 80% and 90% (Edwards et al 1988). The bacteria also plays vital role in vermicomposting. Its activity decreases in moisture content lower than 40% and it almost stops in lower than 10% (Tchobanoglous et al 1993)

5.2 Temperature

Earthworm activity, metabolism, growth, respiration, and reproduction are greatly influenced by temperature (Edwards et al 1996). The temperature for the stable development of earthworm population should not exceed 25°C (Sinha et al 2008). Although E. fetida cocoons survive extended periods of deep freezing and remain viable, they do not reproduce and do not consume sufficient food at single digit temperatures. It is generally considered necessary to keep the temperatures preferably 15°C for vermicomposting efficiency and 20°C for effective reproductive vermiculture operations. Temperatures above 35°C will cause the worms to leave the area or if they cannot leave, they will quickly die. Bacterial activity is also greatly depended on temperature as it multiplies by two per each 10°C increase in temperature and is quite active around 15–30°C.

5.3 Aeration

Earthworms are oxygen breathers and cannot survive in anaerobic conditions. They operate best when compost material is porous and well aerated. Earthworms also help themselves by aerating their bedding by their movement through it. E. fetida have been reported to migrate in high numbers from oxygen depleted water saturated substrate, or in which carbon dioxide or hydrogen sulfide has accumulated.

5.4 pH value

The pH value is also one of the important factors affecting the vermicomposting process (Gajalakshmi et al 2004). Epigenic worms can survive in a pH range of 5–9 (Edwards, 1998). The pH of worm beds tends to drop over time. If the food source/ bedding is alkaline, than pH of bed drop to neutral or slightly alkaline and if the food source is acidic than the pH of the beds can drop well below 7. The pH can be adjusted upwards by adding calcium carbonate or peat moss for adjusting pH downward can be introduced into the mix. Although microorganisms which are active in vermicomposting which can maintain their activity even in lower pH of around 4 but recommended pH range for compost is around 6.5–7.5.

5.5 Ammonia and salt content

Earthworms cannot survive in organic wastes containing high levels of ammonia. Worms are also very sensitive to salts and they prefer salt contents less than 0.5% (Edwards et al 2002). However, many types of manures have high salt contents and if they are to be used as bedding, they should be leached first to reduce the salt content, it is done by simply running water through the material for a period of time.

VI. COMMERCIALIZING VERMICOMPOSTING

In light of the pollution issues, government agencies and farmers are seeking new ways to manage and utilize agricultural wastes to beneficial use. Despite claims that rice residues are agricultural wastes, they are rich in silica plant material and are potential sources of plant nutrients (Mandal et al. 2004; Kadam et al. 2000)

As compared to utilizing rice residues as fuel for energy generation through burning, vermicomposting promotes reuse and bio-transformation of organic waste into organic fertilizer, which helps contribute significantly towards sustainable agricultural practices (Yan et al. 2012)

The vermicomposting process has emerged as an environmentally friendly waste management method as well as an attractive alternative to chemical fertilizers by converting organic detritus into high-quality organic fertilizers. Generally, vermicomposting can accelerate the stabilization process of organic materials through the joint action of earthworms and microorganisms (Sim and Wu 2010).

The proposed system can be divided into four main categories and follows the flow diagram as shown below.

1. Collection of Rice Residue
2. Transport
3. Vermicomposting
4. Packing

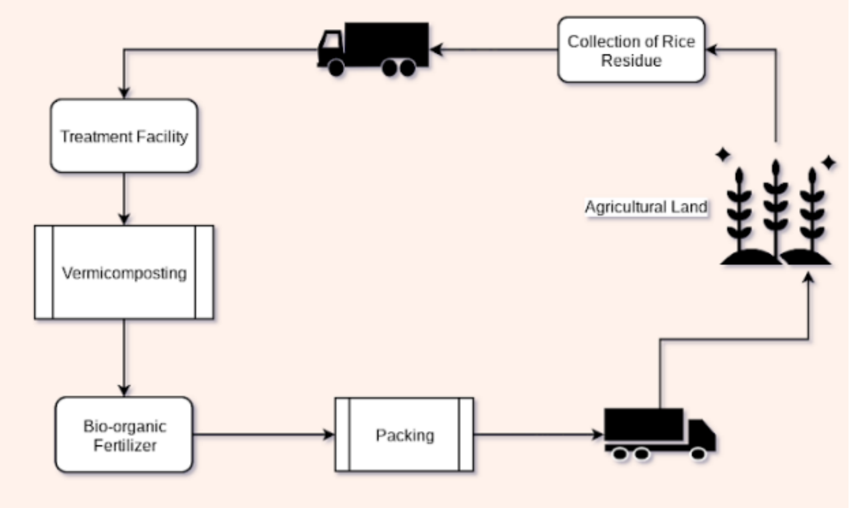


FIGURE 5: Process Flow diagram showing the schematics of the proposed solution.

VII. DISCUSSION AND RECOMMENDATIONS

Increasing generation of solid waste, whether from domestic, agricultural, or industrial sources, has created serious environmental threats. This excessive waste must be recycled and re-incorporated into production processes by using vermicomposting technology. Vermicomposting can transform waste into a form of biofertilizer, which is easily stored, handled, and used in agriculture, providing a vital step toward sustainable organic farming. Vermicomposting is an integrated approach that can be used effectively to improve soil health and crop productivity, to treat wastewater, and to produce energy. It provides favorable conditions for microbes and earthworms to interact and convert waste into biofertilizer. It is suggested as a sustainable technology for waste management, and it can lead to zero waste production. It can also reduce groundwater contamination and the toxicity of soils and plants by removing harmful chemicals.

As a non-homogenous and multiphase reaction system, vermicomposting can not be mathematically modeled. Modeling the vermireactor as a simple CSTR based on assumptions of a homogenous reaction is theoretically incorrect, however it does provide a simple insight into the operation of the reactor as a whole. Earthworm's gut has been modeled as a PFR successfully based on the experimental data by Kiyasudeen et al. Essentially one can argue that the vermireactor is a combination of multiple small PFR systems operating in series. It is recommended that with further research and experimentation, a more practical model for the system can be developed.

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The Influence of Inoculation with *Streptomyces Albogriseolus*-89 on Durum Wheat (*T. Durum* Desf.) Growth and Development

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***Abstract*— *The influence of actinomycete strain Streptomyces albogriseolus-89 (isolated from soils of Khevi region, Stepantsminda, Georgia) on growth and development, as well as the content of metabolites (chlorophylls, carotenoids, anthocyanins, ascorbic acid, proline, soluble phenols, total proteins, soluble carbohydrates) and peroxidase activity in leaves of durum wheat (T. durum Desf.) has been studied. It was established that inoculation of wheat seeds with the strain has stimulated stem and ear growth, positively affected protein content (raised by 12%) and peroxidase activity (increased by 1.3 times) as well as enhanced the yield and resistance of plant to biotic and abiotic stresses.*

***Keywords*— antioxidants, durum wheat, inoculation, Streptomyces albogriseolus-89.**

I. INTRODUCTION

Food supply of the world population is an ecological problem of an international scale. Raising the yield of food crops is one of the ways of the problem's salvation. For this purpose, environmentally safe alternative to chemical fertilizers - the biofertilizers, which are biopreparations made from living microorganisms, are successfully used in agriculture today. After the treatment of seeds or underground parts of the plant with such biofertilizer, the microorganisms of the biopreparation settle on the rhizosphere or inside of the plant and reveal a visible effect on its growth and development; this allows obtaining ecologically safe harvest along with the increase in productivity. In addition to direct effect, microorganisms reveal indirect influence on plant, protecting it from damage caused by various pathogens or abiotic stressors (Miliute et al., 2015). Accordingly, the demand for microbial inoculants and biofertilizers has increased significantly in recent decades. (Thomas, Singh, 2019; Umesha et al., 2018).

Among the promising microorganisms applied in agriculture are actinomycetes, which are producers of many commercially important metabolites, like enzymes, hormones, or antibiotics (Nagendran et al., 2021). Both the rhizosphere and tissues of plants are abundantly populated with actinomycetes. The secondary metabolites produced by these microorganisms improve soil fertility and plant mineral supply, as well as protect the plant from phytopathogens and increase its stress resistance (Silva et al., 2022).

Despite the great biotechnological potential of actinomycetes, the share of products based on these microorganisms on the world market is very small (Silva et al., 2022).

The purpose of the presented study was to investigate the effect of inoculation of durum wheat (*T. durum* Desf.) seeds with the local actinomycete strain - *Streptomyces albogriseolus-89* on the growth and development of the plant, and on the content of metabolites (chlorophylls, carotenoids, anthocyanins, ascorbic acid, proline, soluble phenols, total proteins, soluble carbohydrates) as well as peroxidase activity in leaves.

The strain *Streptomyces albogriseolus-89* was chosen as a test object because of its positive characteristics: high activity of prostaglandin synthetase and the active synthesis of polyunsaturated fatty acids. In addition, its antagonistic activity against a number of microorganisms, including plant pathogens such as: *Elitrosporangium brasiliense, agrobacterium tumefaciens, Aspergillus niger, Pectobacterium aroideae, Xanthomonas campestris,* has been established (Mamulashvili, 1995).

II. MATERIALS AND METHODS

2.1 Research area

The field trial was conducted on the experimental plot of the National Botanical Garden of Georgia, which is located at 700-800m above sea level; soils here are dark-brown, dry, loose, fine-grained, loamy (Urushadze, Blum, 2013). The weather is moderately warm, transitioning from steppe to moderately humid subtropical; according to general features - subtropical-semiarid (with elements of sub-Mediterranean climate). Winter is moderately cold, summer is hot. The average annual temperature is 12.7°C, the average temperature in January - +0.9°C, and in July - +24.4°C; The absolute minimum temperature -23°C, the absolute maximum - +40°C. The average annual amount of precipitations is 560 mm (Elizbarashvili, 2017).

Durum wheat (*T. durum* Desf.) seeds were provided by the Genetic Resources Laboratory of the Institute of Botany, of Ilia State University.

The actinomycete strain *Streptomyces albogriseolus-89* was taken from the collection of the Department of Microbiology of the Institute of Botany of Ilia State University. The strain was isolated from the soils of Stepantsminda district - Khevi.

Cultivation of *Streptomyces albogriseolus-89* was carried out on solid synthetic area of Krasilnikov (CP-I), for 7 days at 28^{o}C in a thermostat (Zvyagintsev, 1991; Pandey et al., 2011). The microbial biomass obtained by cultivation was scraped off the surface of the nutrient medium and dissolved in water at the ratio: 1 g of biomass: 100 ml of distillate. Seeds, for inoculation, were kept in this suspension for 24 hours before sowing.

Both control (untreated) and experimental (inoculated) seeds were sown in triplicate on $4m^2$ (2mx2m) plots (1000 seeds per plot). During the vegetation period, the height and ear length of the test plants were measured; at the end of vegetation the weight of one thousand grains was recorded. The study of metabolites in wheat leaves during the stem elongation phase was carried out by methods described below. For experiments were taken mature, fully expanded leaves of the same age. Each index was determined in triplicate.

2.2 Biochemical assays

2.2.1 Plastid pigments

Chlorophyls and carotenoids were determined spectrophotometricaly. Fresh leaves (100-200mg) were mashed with sand and $CaCO_3$ and washed with ethanol. Optical density of the filtrate was measured (spectrophotometer SPEKOL 11, KARL ZEISS, Germany). Concentration of chlorophylls a and b, also carotenoides was calculated by the formula of Wintermanns (Gavrilenko et al., 1975).

2.2.2 Anthocyanins

100mg of grinded leaves were added with 20 ml of 96% acidified (with 1% HCl) ethanol (99:1). After 24h retention in dark the optical density at 540nm was measured (spectrophotometer SPEKOL 11, KARL ZEISS, Germany) (Ermakov, 1987).

2.2.3 Ascorbic acid

A titration method was used to measure the content of ascorbic acid in plant material. 2 g of fresh leaves were mashed in 15 ml of 2% hydrochloric acid and 10 ml of 2% metaphosphoric acid, and filtered. One ml of the filtrate was added to 25 ml of distilled water and titrated with a 0.001 M solution of dichlorphenolindophenole (Ermakov, 1987).

2.2.4 Proline

0.5 g of dry leaves were mashed in 10ml of 3% sulphosalicylic acid and filtered. 2 ml of the filtrate was added to 2 ml of acid ninhydrin and 2 ml of ice acetic acid. After 1 h exposition on a water bath the extract was cooled and added with 4 ml of toluene and divided in a separating funnel. Optical density of upper layer was measured on a spectrophotometer (SPEKOL 11, KARL ZEISS, Germany) at 520 nm (Bates et al., 1973).

2.2.5 Total phenols

A 0.5 g of fresh leaves was boiled in 80% ethanol for 15 min. After centrifugation the supernatant was saved, and residues of leaves were mashed in 60% ethanol and boiled for 10 min. Obtained extract was added to the first supernatant and evaporated.

The sediment was dissolved in distilled water. One ml of the received solution was added with the Folin-Ciocalteu reagent and optical density was measured at 765 nm. The chlorogenic acid served as control (Ferraris et al., 1987).

2.2.6 Total protein assay

Content of proteins was determined after Lowry (1951).

2.2.7 Soluble carbohydrates

Content of soluble carbohydrates was tested with anthrone reagent (Turkina and Sokolova, 1971). To 100mg of air-dry leaf material was added 96° alcohol for extraction (3-fold). The total amount of the obtained extract was evaporated on a water bath and dissolved in 5ml of distilled water. To 0.5ml of the tested water extract was added 2ml of anthrone reagent and heated in a water bath for 10min. After this procedure the test-tubes were placed in a cold water bath and 15min later the optical density of the solution was measured at 620nm with a spectrophotometer (SPECOL 11, KARL ZEISS, Germany).

2.2.8 Enzyme assay

Peroxidase activity was determined spectrophotometrically: optical density of the products of guaiacol oxidation was measured at the wave length of 470nm by the spectrophotometer (SPEKOL 11, KARL ZEISS, Germany) (Ermakov, 1987).

2.2.9 Statistical processing of data

One way ANOVA and Tukey's multiple comparison tests were used to test differences between the means. All calculations were performed using statistical software Sigma Plot 14.5.

III. RESULTS AND DISCUSSION

Actinomycete inoculation of wheat seeds stimulated both stem and ear growth in test plants (p=0.01) (Fig. 1). The weight of one thousand grains in the experimental variant was also statistically higher, compared to the control (p=0.04); i.e. Seed inoculation with *Streptomyces albogriseolus-89* has a stimulating effect on plant growth and yield (Fig. 1).

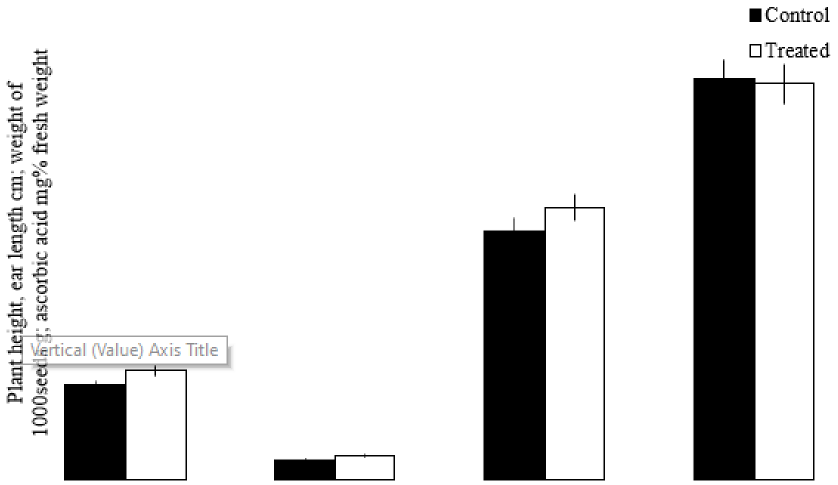

FIGURE 1: Influence of durum wheat (*T. durum* Desf.) seeds inoculation with Streptomyces *albogriseolus-89* on stem and ear length, weight of 1000seeds and leaf ascorbic acid content

It is generally known that the positive effect of plant growth-stimulating actinomycetes on the host plant is due to two main reasons: they supply the plant with growth-stimulating hormones and improve mineral uptake, be it nitrogen fixation, phosphorus solubilization, or siderophores formation (Silva et al., 2022). The stimulating effect of the used strain on the growth and development of test plants may be explained by the similar reason. Particularly which hormone or siderophore is produced by *Streptomyces albogriseolus-89* is a matter for future research.

A powerful photosynthetic apparatus is one of the principal conditions for high plant productivity (Stasik et al., 2016). The efficiency of the photosynthetic apparatus is evaluated according to the amount of chlorophylls and carotenoids (Lichtenthaller, Buschmann, 2001). The study of plastid pigments in leaves of tested plants revealed the statistical similarity (p=0.1) between the experimental and control variants; while the content of carotenoids in the actinomycete-treated plants decreased by 18% (p=0.01) (Fig. 2).

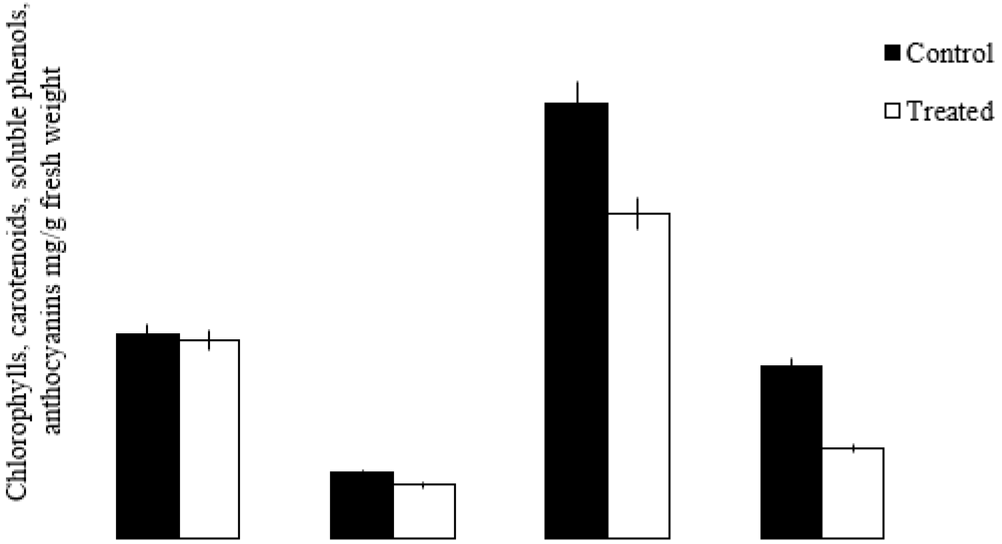

FIGURE 2: Influence of durum wheat (*T. durum* Desf.) seeds inoculation with Streptomyces *albogriseolus-89* on leaf chlorophylls, carotenoids, anthocyanins and soluble phenols content

By the content of carotenoids as antioxidant compounds, it is possible to judge the degree of stress, affecting the plant as well as the degree of plant resistance to this stress (Strzalka et al., 2003). Decrease in carotenoids in inoculated plants can be considered as an expression of the positive effect of inoculation. In hot summer, when the temperature reaches 40°C, which is combined with strong insolation and water deficit, the plants appear under severe stress. If under such conditions, inoculation with actinomycete leads to the reduction of carotenoids as protective antioxidant compounds, it should be assumed that inoculation caused alleviation of the stress negative effect on the expense of microorganism-produced metabolites.

It is known that plants have evolved physiological and biochemical mechanisms of stress resistance. Among them the antioxidant system represented by enzymes and low-molecular antioxidant compounds is particularly important (Li, and Liu, 2016; Laxa et al., 2019). Most of the metabolites studied in experimental plants are antioxidants. We thought that their quantitative study would give some idea about the influence of microbial origin compounds on the physiological state of the plant under the stressful summer conditions (high temperature, intensive insolation, lack of water).

It is established that ascorbic acid plays one of the main roles in protecting the photosynthetic apparatus from stress (Venkatesh, et al., 2014). Under stress conditions its content increases in plants (Yang et al., 2008). From the obtained results it is clear that the content of ascorbate in leaves of inoculated plants was statistically similar to the control variants ($p>0.05$) (Fig. 1).

Phenolic compounds play an important stress-protecting role in cell (Winkel-Shirley, 2002; Cesar, Fraga, 2010). A number of studies have shown the accumulation of phenols in plants under stress conditions (Sharma et al., 2019). A 33% reduction of these compounds was mentioned in the inoculated plants compared to the control ($p=0.02$) (Fig. 2).

One group of phenolic compounds - anthocyanins, acts as a light screen and protects chlorophyll from damage by excess light (Gould et al., 2018). It has been established that under various stress conditions, the accumulation of anthocyanins in vegetative tissue increases (Gould et al., 2018; Kamjad, et al, 2021). In our experiments the content of anthocyanins in the inoculated variants decreased by 1.9 times compared to the control ($p=0.04$) (Fig. 2). It should be assumed that the reduction of both soluble phenols and anthocyanins in actinomycete-treated plants may be due to the positive effect of actinomycete's metabolites.

It is well known that so-called osmoprotectants are also involved in plant protection against stress. Among them are free amino acids, soluble carbohydrates and proteins. They protect the membrane protein-lipid components from various stresses (Iqbal et al., 2020).

Amino acid proline and soluble carbohydrates are osmoprotectants that retain water in the cell and keep its turgor. Their positive role in plant resistance to water deficit has been emphasized in many works. (Ashraf et al., 2018; Laxa et al., 2019). At the same time, soluble carbohydrates reliably protect proteins from denaturation and provide membrane stability (Mohammadkhani and Heidari, 2008).

Obtained results clearly demonstrate that the content of both proline and soluble sugars in leaves of inoculated plants was statistically identical to the control variants (p=0.2). It can be assumed that the compounds produced by the inoculum do not significantly affect the metabolism of osmolytes (Fig. 3).

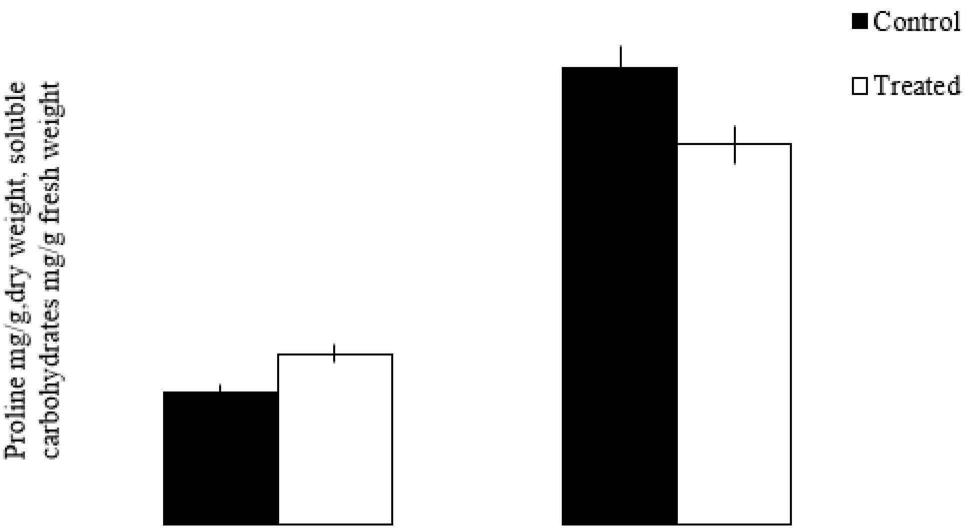

FIGURE 3: Influence of durum wheat (*T. durum* Desf.) seeds inoculation with Streptomyces *albogriseolus-89* on leaf proline and soluble carbohydrates content

Inoculation of wheat seeds with *Streptomyces albogriseolus-89* positively affected the protein content in leaves of experimental plants - this index increased by 12% (p=0.04) (Fig. 4).

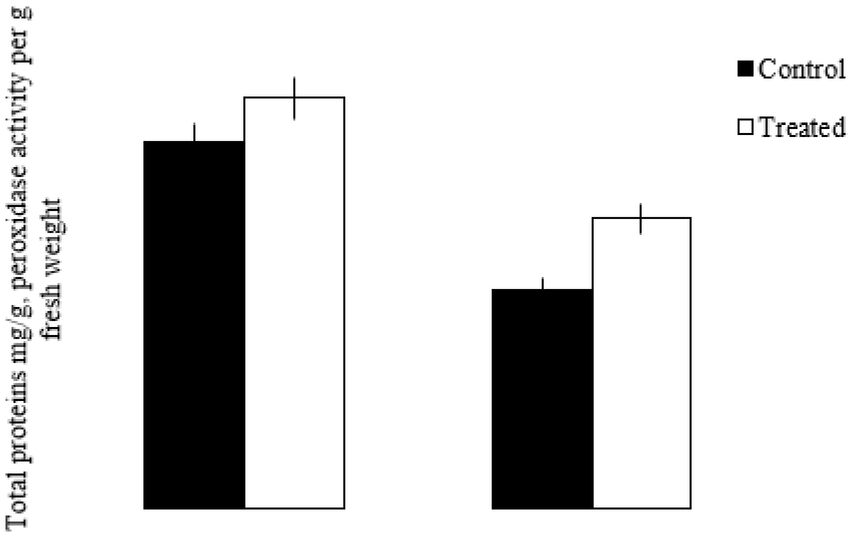

FIGURE 4: Influence of durum wheat (*T. durum* Desf.) seeds inoculation with Streptomyces *albogriseolus-89* on leaf peroxidase activity and total proteins content

It is known that the qualitative and quantitative composition of plant proteins changes under unfavorable conditions; The synthesis of stress proteins - dehydrins is activated, which act like osmolytes and participate in the stabilization of membrane proteins and osmotic regulation (Iqbal et al., 2020; Mohammadkhani and Heidari, 2008). Experimental results demonstrate a positive effect of microbial compounds on protein synthesis, which contributes to the plant's resistance to adverse environmental conditions. A 1.3-fold activation of antioxidant enzyme - peroxidase in inoculated leaves (p=0.003) can be considered as proof to this (Fig. 4).

Peroxidases (EC 1.11.1) are a large group of enzymes, ubiquitous in the cell and have various functions in plant metabolism (Passardi et al., 2005). In particular, they take an active part in plant growth and development, regulation of auxins and phenolic compounds amount, adaptation to unfavorable conditions, etc. (Graskova et al., 2010). It has been established that the activity of antioxidant enzymes, including peroxidases, is high in drought-resistant plants (Laxa et al., 2019; Kapoor et al., 2020).

The activation of peroxidase in leaves of inoculated plants should be considered as an expression of positive effect of *Streptomyces albogriseolus-89*, supporting plant resistance to stress.

IV. CONCLUSIONS

Obtained results clearly demonstrate that the inoculation of wheat seeds with *Streptomyces albogriseolus-89* strain has a stimulating effect on plant growth and development, increases its productivity and resistance to biotic and abiotic stresses. Accordingly, the potential of the strain may be used to make a plant growth stimulating preparation; for this purpose additional research is planned in future.

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Stoichiometry and Kinetics of Hydroxyl Radicals in Air Quality

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Abstract— *The environmental health that nature offers us every day is closely linked to the sanitization provided by atmospheric chemistry, due to the oxidative processes that occur under the powerful sunlight passing through the clouds and reaching the forests, oceans, and seas, performs the multiple reactions, recombinations, mineralizations, degradations etc. in the atmosphere. It is a chain reaction called Open Air Factor (OAF) that cleans and disinfects the environment in which all living beings live called the biosphere.*

There are technologies and elements necessary to be able to imitate nature in this process of environmental sanitization for indoor environments based precisely on the Open Air Factor (OAF), and for this, for a question of safety and efficiency, it is necessary to measure the quantitative proportions or mass ratios of the chemical elements involved and that are involved in this natural chemical reaction, as well as to study the proportion of the various resulting elements and the composition of chemical mixtures of the components.

The comparison of this stoichiometry that nature provides us with similar artificial systems for interiors will give us a vision of how similar the processes and resultants are.

This paper is based on the stoichiometry and kinetics of hydroxyl radicals emitted by a device technologically based on the Open Air Factor (OAF) aimed at controlling indoor air quality.

Specifically, it has been the analysis of the decay of the number of molecules of hydroxyl radicals (OH·) when reacting in the presence of typical air pollutants such as CO2, hydrocarbons and bicarbonate ions. These amounts of hydroxyl radical molecules (OH·) under study, unlike the multiple reactants that exist in Nature, have been generated with only two reactants, hydrogen peroxide and ozone, following current international safety regulations regarding their emissions in the presence of people.

Keywords— Hydroxyl radicals (OH·); Volatile Organic Compounds (VOC's), Advanced Oxidation Process (AOP's, Indoor Air Quality (IAQ), Indoor Air Pollution (IAP), Open Air Factor (OAF), reactive oxygen species (ROS's).

I. INTRODUCTION

Air quality is closely related to good health. Although in general terms more importance has been given to outdoors air quality, due to urbanization, humans now spend more than 90% of their time indoors (**Figure 1**), which corresponds to more than 10,000 liters of air breathed per day.

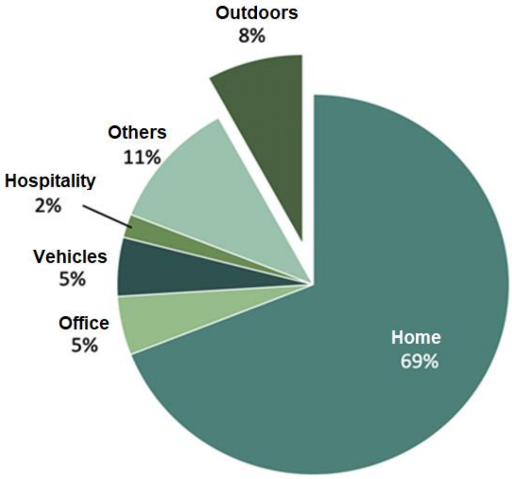

FIGURE 1: Fraction of average time spent in each space in a day according to US Environmental Protection Agency data [1]

Indoor air can be up to ten times more polluted than outdoors resulting in poor Indoor Air Quality (IAQ), which poses a risk for the development or worsening of diseases as well as decreased productivity (resulting in economic charges) [1] [2]. Nearly 4 million people die each year from illnesses attributed to indoor air pollutants (IAP), which can exacerbate pre-existing acute allergy-type diseases such as dermatitis or rhinitis, and play a role in the development of respiratory diseases such as pneumonia, asthma or chronic obstructive pulmonary disease (COPD) and non-respiratory diseases such as heart attacks or cancer [3] [4]. IAPs include biological agents (viruses, bacteria, and fungi), as well as chemical agents and combustion products, the most relevant being particulate matter (PM) (e.g. smoke), volatile organic compounds (VOCs), carbon oxides (COx), nitrogen (NOx) or sulfur (SOx), radon and ROS (Reactive Oxygen Species).

Ozone is one of the ROS and this gas can be emitted from any type of household appliance or device (e.g. microwave, television, photocopier, oven, discharge lamps such as tubular fluorescent lamps) by means of the so-called corona effect. This effect is an electrical phenomenon produced by the ionization of the gas surrounding a charged conductor. It occurs spontaneously on high-voltage lines and manifests itself in the form of a luminous halo [5] [6].

Due to the oxidation reactions generated by ozone in organic compounds (especially terpenes, present in perfumes and cleaning products), secondary non-volatile organic compounds are produced in aerosols (SOA) even more dangerous than the primary ones [2] [7] [8] [9].

Although air does not contain indigenous microbiota, it acts as a dispersal medium for a large number of microorganisms such as may be the cause of the recent Sars-CoV2 pandemic. Most microorganisms (including bacteria, viruses and fungi) are transmitted by bioaerosols, airborne particles that are dispersed in the air and when expelled (e.g. by talking, coughing, sneezing, etc.) contain more than 90% water, which evaporates according to the temperature and relative humidity of the environment until it is reduced in size and consists of microorganisms or parts of microorganisms and inorganic ions [10].

The IAQ is highly dependent on three factors [8] [11]:

(1) the activities carried out by the occupants (e.g. emission of tobacco smoke, fragrances, cleaning products, cooking odors). Individually, we can contribute to improving the IAQ at home by reducing the source of pollutants, i.e., controlling the activities we carry out to minimize their emissions, although this is not always possible.

(2) the intrinsic characteristics of the building (e.g. building materials, furnishings, ventilation capacity, presence of air conditioners). There is a set of symptoms and diseases attributed to poor IAQ called "building related illnesses", which are divided into Building related illness (BRI) if the causative agent can be identified, usually biological (e.g. legionellosis) but can also be chemical (e.g. hypersensitivity pneumonitis) or, in Building related illness (BRI) if the causative agent can be identified, usually biological (e.g. legionellosis) but can also be chemical (e.g. hypersensitivity pneumonitis). Sick Building Syndrome (SBB) if general environmental contamination is the trigger for the symptoms, which include irritation of mucous membranes (e.g. eye), neurotoxic effects (e.g. fatigue), asthma and the like (e.g. chest tightness) among others.

(3) Outdoor air since the quality of renewed air depends on it. Although indoor air is usually more polluted than outdoor air and therefore natural ventilation of spaces is recommended, 99% of the population lives in spaces where the recommended limits of pollutants in atmospheric air are exceeded, resulting in a problem to ensure good IAQ in these spaces [12]. In fact, recent studies have linked poor air quality in cities to increased infectious disease transmissibility, specifically on the risk of Sars-CoV2 infection [13].

Due to public awareness of the detrimental effects of breathing polluted air, technologies have emerged to reduce contaminants (both biological and chemical) in these spaces, such as HEPA filters. The recent pandemic has exacerbated this concern and makes it imperative to find ways to ensure good indoor air quality in a manner that is safe for occupants and independent of outdoor air renewal.

1.1 THE OH·

The generation of OH· as well as other superoxides by different methods, called advanced oxidation processes (AOP), was first studied by NASA in the 1990s, in order to be used to avoid the accumulation of organic compounds on spacecraft during space travel [14]. The evaluation of the role of OH· in the decomposition of these compounds showed that it also participates in the inactivation of microorganisms and the elimination of inorganic pollutants. Since then, a large amount of scientific literature has corroborated the use of AOPs for the treatment of pollutants and microorganisms, first in water and later in air and surfaces. AOPs include all those methods of OH^- generation that aim to generate an oxidizing environment allowing the mineralization of pollutants (organic and inorganic) and the inactivation of microorganisms [15] [16].

These methods generate OH· and other oxidizing agents mainly by reactions between O_3, H_2O_2, UV and/or a catalyst.

OH· is the most important natural oxidant in tropospheric chemistry, often called a "detergent" because it oxidizes pollutants and microorganisms in the environment. Due to its chemical instability and high oxidative potential of 2,80V (second only to flourine and 2,05 times higher than the potential of chlorine) OH^- is the most reactive species in biology, with an ephemeral half-life of 10^{-9} seconds [17]. Therefore, its synthesis, degradation and consequent local concentration depend solely on the species present in situ around it, with which it reacts rapidly and non-selectively, acting like a spark.

OH· is part of a large number of intercommunicating and dynamic reactions involving species naturally present in the air. Both OH· itself and many of the species in these reactions are Reactive Oxygen Species (ROS), unstable species derived from oxygen that react with others to return to equilibrium. Within ROS we find ions such as hydroxide anion (OH^-), free radicals such as superoxide anion (O_2^-) and precursor species of instability, such as hydrogen peroxide (H_2O_2) (**Figure 2**). These species generate cascades of biochemical electron transfer reactions (oxidation and reduction) where other ROS and secondary species are generated [7] [15] [18] [19] [20]. All this contributes to a generalized oxidizing environment in space, as instability spreads from molecule to molecule.

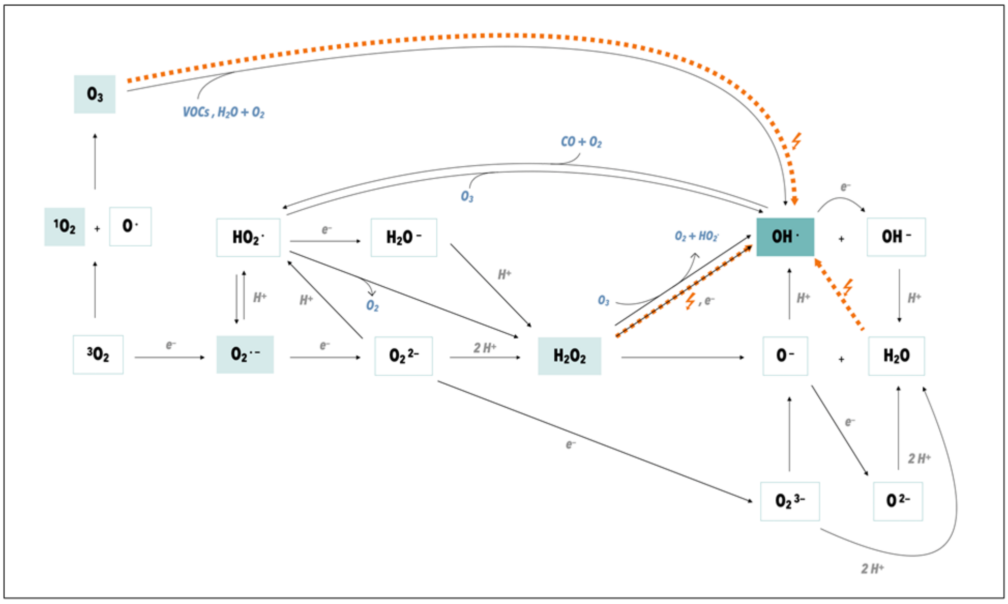

FIGURE 2: Simplified representation of the reactions between ROS taking place in atmospheric air. [Own source]

In the 60s it was determined that rural air had powerful germicidal properties, termed Open Air Factor (OAF). Druett et al. attributed this ability to the ozone-olefin complex, an organic compound previously identified in the composition of air that we now refer to as an alkene (hydrocarbon with double bonds) [21]. A couple of years later, Dark et al. verified that peroxide hybrid ions (now known as Criegee biradicals) formed in the ozonolysis of various alkenes were responsible for the significant but variable inactivation of two microorganisms and thus the active agent of OAF [22]. Very little work has been done on AOF since then, and although the disinfection capacity of AOF (greater than that of ozone) has been confirmed, no further information on the identity of the active agent has been provided [23] [24] [25].

According to current information, the cycle addition of ozone to an alkene (both in the gas phase) attacks the double bond and forms an unstable primary ozonide, which evolves generating radical intermediates called Criegee biradicals [26]. Although biradicals can theoretically decompose via three pathways, evidence rules out two of them occurring naturally in the environment: the removal of an oxygen atom from their structure is not feasible at room temperature and pressure, and radical formation, a consequence of the rearrangement of the biradical into an unstable ester, has not been detected [27] [28]. The decomposition of the biradical by the remaining pathway, through its rearrangement into a hydroperoxide, is considered an important source of generation of hydroxyl radicals (OH·), the major natural oxidant in the troposphere [29]. Could OH· then be the active agent of OAF?

1.2 THE OXIDATION

Chemically OH· is a free radical, which together with ions are the two main sources of chemical instability. Both species present anomalies in electrons and to return to equilibrium they need to react with others, which generates a cascade of instability in which other species, called instability precursors, participate. Ions present charge imbalance in their chemical structure, they have either an excess or a deficit of electrons: those species that have lost electrons (the cations) are electropositively charged (oxidized), while those that have gained electrons (the anions) are electronegatively charged (reduced). It is a dynamic and compensated system: due to the theft of an electron, one species is in the reduced (-) state when it leaves another in the oxidized (+) state. On the other hand, free radicals have a spin imbalance in their structure, i.e. they have some unpaired electrons, so they are much more reactive than ions. Radicals are electrically neutral by itself, so they do not seek to compensate their charge, but quickly steal an electron to compensate their spin, oxidizing without selectivity.

OH· react with organic compounds in 3 different ways:

(1) by electron transfer, generating charge imbalance in the molecule with which it reacts and allowing the formation of new bonds and links. Finally, these structures lose their conformation and three-dimensional structure.

(2) by addition to aromatic rings or double or triple bonds in unsaturated hydrocarbons, which breaks these bonds and generates an alcohol radical (-OH) in the chain. These unstable radicals in organic compounds are incorporated in the classical oxidation pathway, until they become mineralized: the structures lose organic matter in the form of carbon dioxide (CO_2) (**Figure 3**) [30].

(3) by abstraction of a hydrogen in saturated hydrocarbons, resulting in a water molecule and a free alkyl radical (R·) in the organic compound [31]. The presence of an alkyl radical initiates the peroxidation process, where by incorporation and interaction of species a positive feedback of irreversible damage is generated in the molecule. Other radicals can also form in the chain (e.g. alkoxy radicals (RO·)) that are transformed by decomposition, isomerization or hydrolysis, leading to the formation of oxygenated compounds (e.g. alcohols, carbonyls (aldehydes or ketones), carboxylic acids) that are incorporated into the classical oxidation pathway (**Figure 3**) [9] [32].

The remaining CO_2 present at the end of these mineralizations is eventually transformed into carbonate or bicarbonate, oxygen and water, depending on the ambient humidity. This degradation is related to an indirect reaction between OH· and CO_2, which occurs by the instantaneous uptake of an electron by the radical (part of the Fenton process) in an environment contaminated with NO_2. The resulting hydroxyl anion (OH^-) is responsible for the formation of carbonate ions upon reaction with CO_2 [33].

$$NO_2^- \rightarrow NO_2 \cdot + e^-$$

$$OH \cdot + e^- \rightarrow OH^-$$

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O$$

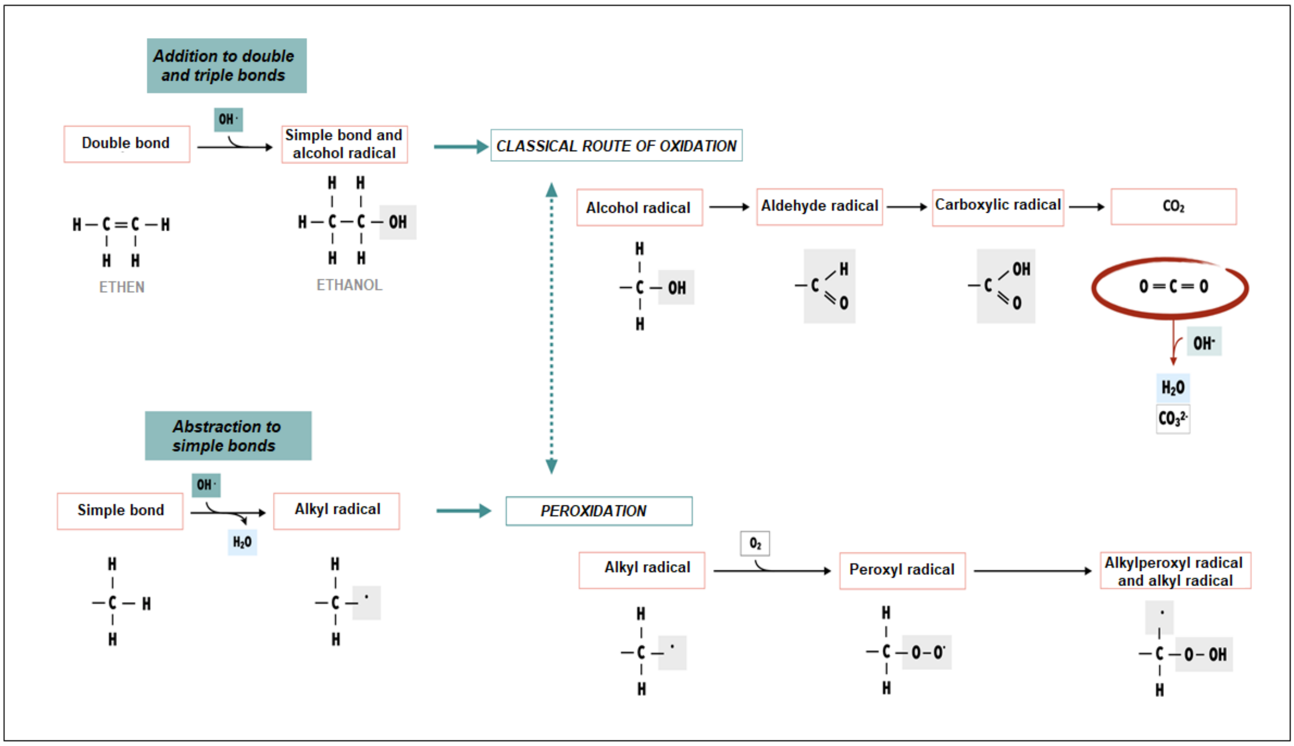

FIGURE 3. The incorporation of an oxygen molecule (O_2) into the alkyl radical (R·) gives rise to the peroxyl radical (ROO·) in the organic compound, which can subsequently isomerize by stealing the hydrogen from a nearby carbon, transforming it into a hydroperoxide radical (ROOH) and generating another alkyl radical in the chain (R·). [Own source]

1.2.1 Mineralization, transformation, and precipitation of pollutant compounds

Due to the relevance of IAQ control, WHO developed guidelines recommending safe exposure limits for selected HAPs: formaldehyde and other VOCs (benzene, naphthalene, benzo[a]pyrene, trichloroethylene and tetrachloroethylene), radon, particulate matter (PM), carbon monoxide and nitrogen dioxide [4].

VOCs include all those hydrocarbons ("organic compounds") that occur in a gaseous state ("volatile") at room temperature. OH· reacts with them by abstraction and addition, mineralizing them and decreasing their concentration indoors. Among the VOCs, the most important are **alkenes**, due to the danger that their accumulation poses to health, as well as the SOAs generated by their reaction with ozone, which is attacked by OH· through addition or abstraction of a hydrogen, initiating its mineralization; **formaldehyde**, one of the SOAs generated by ozonolysis, especially of terpenes and highly flammable, with a strong and penetrating odor, soluble in water and very volatile, which is incorporated in phase 3 of the oxidation cascade of organic compounds (**Figure 3**); and **odoriferous molecules**, lipophilic and small chemical compounds perceptible by our sense of smell that usually contain nitrogen in addition to hydrogen and carbon, which due to the presence of nitrogen we will also obtain ammonia or another similar compound as a product of mineralization [34]. Due to its high reactivity, the reaction time of OH· for the mineralization of most VOCs is generally shorter than the corresponding time for other oxidizing agents such as NO_3 radicals and ozone, reducing the mineralization time of some organic compounds from years to days, even hours (**Table 1**).

TABLE 1
HALF-LIFE OF SOME VOCS WHEN REACTING WITH OH·, NO_3^- AND O_3 IN THE GASEOUS STATE [35].

VOC	Lifetime due to reaction with:		
	OH· radicals	NO_3 radicals	O_3
Acetaldehyde	8.8 hr	17 d	>4.5 yr
Acrolein	6.9 hr	4.2 d	57 d
Benzene	9.4 d	>4 yr	>4.5 yr
Ethane	47 d	>12 yr	>4500 yr
Ethanol	3.6 d	23 d	--
Ethene	1.4 d	225 d	10 d
Formaldehyde	1.2 d	80 d	>4.5 yr
n-Octane	1.3 d	240 d	>4500 yr
Phenol	5.1 hr	9 min	~50 d
Propane	10 d	7 yr	>4500 yr
Propene	5.3 hr	4.9 d	1.6 d
Styrene	2.4 hr	22 min	1.0 d
Toluene	1.9 d	1.9 yr	>4.5 yr

On the other hand, OH· interacts with rhodon gas and PM (suspended volatile particles generally of undetermined composition of sulfates, nitrates, ammonia, sodium chloride, elemental carbon, mineral dust, water and even inorganic compounds such as dust or sand) by electron transfer, being electrostatically captured and agglomerated by its strong electrostatic charge, and subsequently precipitated to the ground with a sufficient size to be collected. In addition, the accumulation of carbon, nitrogen and sulfur oxides is prevented by promoting their natural cyclic oxidation [34].

1.2.2 Inactivation of microorganisms

Microorganisms, as well as all living matter, are made up of organic molecules (mainly hydrocarbon chains (H-C)) that are mineralized by a sequence of free oxidative reactions to obtain mainly CO_2, O_2 and H_2O. Although OH· acts non-selectively on all microorganisms present in water, air and surface, the morbid effect of OH^- on each of them is due to their sensitivity to oxidation [36]. This sensitivity depends on which organic macromolecules make up its outermost structures and which, therefore, interact with the environmental OH·. There are 4 groups of macromolecules: the nucleic acids that make up the genetic material and the glucids, lipids and proteins that make up the structures that surround it. Of these last three, lipids and proteins are the macromolecules sensitive to oxidation.

According to their outermost layer, viruses can be non-enveloped (they present a protein capsid) or enveloped (over the capsid there is a lipid bilayer with glycoproteins); bacteria are classified as gram-positive (they present a thick proteoglycan wall) and gram-negative (over the wall there is a lipid bilayer with lipopolysaccharides); while fungi and yeasts (unicellular fungi) present in their outermost layer a wall formed by chitin and glucans from which glycoproteins protrude (**Figure 4**) [37].

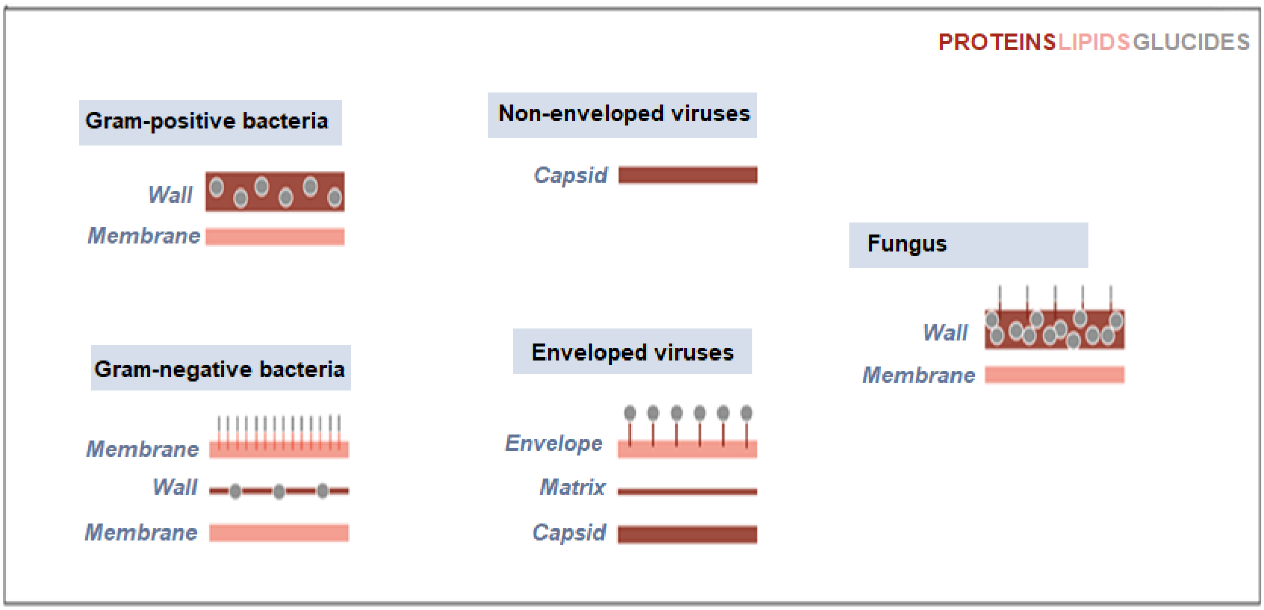

FIGURE 4: Structural composition of pathogens. [Own source]

Lipids are mainly composed of unsaturated hydrocarbon chains that react with OH· either by addition breaking the double and triple bonds generating alcohol radicals (-OH) that will be incorporated into the oxidation pathway or by abstraction of a hydrogen generating alkyl, peroxyl and finally hydroperoxides radicals. Mineralization and peroxidation of lipid membranes modify their spatial distribution and consequently their structure. On the other hand, **proteins** are composed of amino acids and OH· can alter their charges by electron transfer. This modifies their 3D structure and leads to protein fragmentation and can form disulfide (covalent) bonds between amino acids, resulting in intra- and interprotein bonds, so that the protein loses its conformation. In both cases, proteins form aggregates and lose their correct structure.

These irreversible structural alterations created in lipids and proteins through OH· promoted oxidation lead to the loss of the integrity of the structures that envelop the microorganisms, and consequently the loss of their viability and functionality.

II. MATERIALS Y METHODS

2.1 Selection of Items

The literature review was carried out using the PubMed website, aiming to answer the question formulated at the beginning of this study: **What are the main atmospheric reactions involved in the formation of hydroxyl radicals from advanced oxidation processes, and how do they evolve over time?**

The search strategy for scientific articles on the use of OH· as a participating agent in advanced oxidation processes, both for the mineralization of volatile organic compounds and the inactivation of microorganisms, was divided into two main criteria in order to find scientific evidence for the guarantee of a high indoor air quality.

The first criterion was based on focusing the search on atmospheric oxidation processes involving ozone, since it is one of the main pathways for reactions between ROS that occur in air, with the intervention of OH· as an atmospheric detergent. This search could provide information on the proportion of reactants that optimizes the degree of environmental oxidation, as well as the speed of the reaction and information about the reaction products. It is also expected to find a medical device that uses ozone as the initiator of the chain of environmental reactions produced by OH·. Thus, the MeSH Terms used in PubMed were as follows: {atmosphere AND ozone} AND {oxidation reduction}. A total of 91 papers were found.

The second criterion tried to narrow down the atmospheric reactions in the analysis of reactive oxygen species in general, in such a way that the transient evolution and steady-state concentration of OH^- against all reagents and organic compounds present in the air could be estimated, using both stochastic models and real experiments. The outcome of this second search would define the current conception of OH· as a harmless agent and mineralizer of volatile organic compounds, with the aim of guaranteeing environmental quality. In this case, the MeSH Terms used in PubMed were as follows: {atmosphere/chemistry OR atmosphere/metabolism OR atmosphere/analysis} AND {reactive oxygen species}. A total of 38 papers were found.

In both search strategies, the scientific production was also limited to the last 5 years of publication in order to avoid the existence of determinant changes within the field of advanced oxidation processes, in addition to filtering the results by *Abstract*, in order to speed up the analysis of inclusion or exclusion of the paper in the final selection of publications.

In general terms, out of a total of 129 papers, all those following the criteria detailed below were included. The papers should include reactions as close as possible to those found in nature, where OH· arises from the reaction between ozone and hydrogen peroxide, both naturally and photocatalytically initiated. Likewise, reactions of OH· with various common environmental pollutants should also be collected, describing the rate of reaction development. Therefore, any publication that did not include the above information was not considered.

Complementary to the inclusion criteria, the exclusion criteria considered that the study of mineralization of some very particular and rare volatile organic component in the atmosphere was excluded. Finally, the titles referring to oxidation processes in liquid water media were also discarded, since the behavior of the reactions in liquid media is not analogous for the guarantee of a high level of environmental quality.

Once the articles were filtered according to the inclusion and exclusion criteria previously indicated, 37 of the 129 papers were finally selected and classified into the categories shown in Table 2.

TABLE 2
SUMMARY OF THE SELECTION OF SCIENTIFIC ARTICLES PUBLISHED DURING THE LAST 5 YEARS.

Branch of study	Number of selected papers
Stoichiometric study of the reaction of ozone with hydrogen peroxide for the generation of OH· radicals.	7
Kinetic study of OH· concentration versus environmental reactions for the mineralization of volatile organic compounds and hydrocarbons.	11
Other items of general interest for the study.	19

In order to reduce the *risk of bias* and avoid distortion of the outcome of the *systematic review* process, the inclusion/exclusion criteria applied to the papers were obtained from a double parallel review of the entire set of articles, providing titles that had been discarded in the first instance. Likewise, the search of the *papers* aimed to collect the amounts of OH· emitted, thus resulting in a numerical question. The articles found and selected according to the 3 criteria mentioned above reflect the diversity of both natural and laboratory-tested reactions, and provide us with the quantification of the OH· emission, which will be used to give comparative values to the stoichiometric and kinetic calculations proposed in this article.

2.2 Objectives and Hypotheses of Mathematical Formulation

The generic purpose of the present study is to validate two theoretical models about the generation of hydroxyl radicals (hereinafter, OH·), produced by an OAF generator device, and subsequently emitted to the environment. For this purpose, two studies of maximum OH· generation will be carried out in parallel, one stoichiometric in gas phase (study of the reactions produced in the device) and the other kinetic without air renewal (with and without device) only subject to the environmental chain reactions present (study external to the device). The hydroxyl radical emission results of the theoretical model will also be compared with the results of other publications, which report OH· radical emissions.

In both stoichiometric and kinetic studies, mathematical formulas have been used, as well as physical constants and chemical reactions, subject to certain assumptions that will be detailed below.

Specifically, for the stoichiometric study, the three specific objectives consist of: 1º the calculation of the concentration of OH· emitted according to the concentration of the reactants involved, 2º the study of the theoretical efficiency of the reaction and 3º the analysis of the theoretical residues of the reaction. In this stoichiometric study the capacity of the reaction between ozone (O_3) and hydrogen peroxide (H_2O_2) both in gas phase will be analyzed, which will allow to calculate in a theoretical way the concentration of OH· emitted, as well as the presence of the excess quantities of ozone and hydrogen peroxide. This will make it possible to verify compliance with the legal emission limits for these reagents after 8h, whose values are established by international organizations as 1 ppm and 0,05 ppm for hydrogen peroxide and ozone, respectively. Therefore, it is assumed that both reagents will only participate in this reaction, without the intervention of any parallel or parasitic reaction, both in gas phase, to produce hydroxyl radicals in addition to the environmental ones that are always artificially present by default.

Hydrogen peroxide and ozone are present in gas phase. The amount of ozone is controlled by a generator that produces a fixed amount of 0,04 mg/h, while the peroxide has been obtained in gas phase by convective evaporation of a peroxide solution of known purity, by capillarity through a polyester wick that will be responsible for the evaporation. With a volume of 35 mL of solution, a constant evaporation of 0,39 mL/day is measured, based on calculations obtained in previous experiences with the OAF generator device, resulting in a total evaporation time of 90 days. During the stoichiometric calculation process, the density of both reactants in gas phase corresponding to room temperature is considered. Also, the reaction efficiency will be considered as the theoretical yield at stoichiometric level.

On the other hand, the specific objectives for the kinetic study consist of the analysis of the temporal evolution of the concentration of OH· in an environment, starting from the concentration of the usual components of nature. The evolution of the OH· concentration will be estimated over a time period of 30 minutes, starting from the ambient concentrations of the reagents, in a space of 300 m^3 volume occupied by 1 and 50 people and without air renewal, in order to check that the calculation of the artificial generation of OH· is in accordance with its natural generation. This evolution will be compared with an analogous case, where there is an external source of OH· by means of an OAF generating device, where, on the basis of previous experiences, an additional contribution of OH· by the device of $2{,}84\cdot10^7$ molec·$cm^{-3}\cdot s^{-1}$ is assumed. In this kinetic study, the volume is considered to be completely isolated from the outside, and as indicated above, it will be 300 m^3.

The concentration inside the 300 m^3 isolated volume will be based on standard ambient levels of CO_2, VOCs, HC, etc. outdoors. The involvement of OH· with volatile organic compounds, viruses, bacteria, water, hydrocarbons, carbon dioxide, carbonates, bicarbonates, carbon monoxide, oxygen, hydrogen peroxide and ozone, which are involved is considered. Also, the oxidation of carbon dioxide to carbonates and bicarbonates is assumed by the presence of NO_2- ions in the environment, facilitating the production of the Fenton process.

Finally, in the case studies where 1 or 50 people are considered inside the 300 m^3 isolated volume, an additional contribution of carbon dioxide will be considered only, due to the exhalation of the CO_2 people. This extra CO_2 input shall be defined by the average lung capacity of a human being, giving a magnitude to the exhaled volume of air, which includes a small portion of carbon dioxide. The human being shall be considered to be approximately 100 times the inhaled concentration of CO_2 in the instant immediately preceding exhalation.

2.3 Theoretical Model

2.3.1 Stechiometric Study

This section will analyze the ability of the following reaction at stoichiometric level to generate OH· radicals in compliance with the legal emission limits of the reactants both in gas phase. O_3 will be produced by a generator and H_2O_2 will be obtained by convective evaporation of liquid hydrogen peroxide in contact with a polyester wick.

$$O_3 + H_2O_2 \rightarrow OH\cdot + O_2 + O_2H\cdot \tag{R1}$$

In this way, the following physical constants will be considered:

- Volume of liquid hydrogen peroxide: 35 mL.
- Evaporation of hydrogen peroxide: 0,39 mL/day.
- Duration of the hydrogen peroxide tank: 90 days.

In addition, the legal emission limits for each reagent are as follows:

- Maximum exposure time of hydrogen peroxide: 8h (1 ppm).
- Maximum O_3 exposure time: 8h (0,05 ppm).

On the other hand, the degrees of freedom to be used for the study of OH· generation are the following:

- Purity of liquid hydrogen peroxide p, in %.
- Volume of the enclosure area where the reaction takes place V, in m^3.
- Initial O_3 concentration c, in ppm.

The steps carried out to calculate the concentration of OH· emitted according to the concentrations of the reagents, represented as degrees of freedom (c,p and V expressed in ppm, % and m^3, respectively), are shown below, as well as the resulting formula that will allow the OH· concentration to be represented graphically by modifying these values at will.

A. Calculation of the [OH·] emitted according to the concentration of reagents

In order to calculate the concentration of the OH· radical emission, the ozone concentration (initially in parts per million) is first expressed as the concentration of the amount of substance per unit volume, in mol/cm^3. This initial calculation is shown in the following equation, where the density of ozone at ambient temperature has been used:

$$c[ppm_{O_3}] \cdot \frac{\frac{1m^3O_3}{10^6m^3air}}{1[ppm_{O_3}]} \cdot \frac{2{,}14[kg]}{1[m^3O_3]} \cdot \frac{1000[g]}{1[kg]} \cdot \frac{1[mol]}{48[g]} \cdot \frac{1[m^3]}{10^6[cm^3]} = 4{,}167c \cdot 10^{-11}[mol/cm^3] \qquad \textbf{(R2)}$$

Then, the previous value is also expressed per unit of time, using as a reference a value of 8h, representing the exposure time to a certain ppm of ozone:

$$\boldsymbol{c(O_3)} = \frac{4{,}167c \cdot 10^{-11}[mol/cm^3]}{8 \cdot 3600[s]} = 1{,}447\boldsymbol{c} \cdot 10^{-15}[\boldsymbol{mol/(cm^3 \cdot s)}] \qquad \textbf{(R3)}$$

On the other hand, starting from the initial volume of hydrogen peroxide, as well as the density (which, in general, is a function of the peroxide purity), this volume is converted into the amount of peroxide substance at the start of the reaction, as shown in the following equation. Despite conceiving density as a purity-dependent variable, it has been empirically determined that the value of the average or effective density for different purities was found to be approximately invariant, as follows $\rho_{ef} \simeq 1{,}08g/ml$.

$$35[ml_{H_2O_2}] \cdot \rho(p)\left[\frac{g}{ml_{H_2O_2}}\right] \cdot \left(\frac{p}{100}\right) \cdot \frac{1[mol]}{34[g]} \equiv 0{,}011p[mol] \qquad \textbf{(R4)}$$

The concentration of the peroxide involved in the reaction is then expressed per unit volume and time, analogous to the case of ozone. In this case, the volumetric concentration is expressed using the volume of the enclosure area where the reaction takes place. The reference time is the duration of a 35 mL tank of peroxide, which turns out to be 90 days, based on previous experience with the OAF generating device.

$$\boldsymbol{c(H_2O_2)} = \frac{0{,}011p[mol]}{V \cdot 10^6[cm^3] \cdot 90 \cdot 24 \cdot 3600[s]} = 1{,}430\frac{\boldsymbol{p}}{\boldsymbol{V}} \cdot 10^{-15}[\boldsymbol{mol/(cm^3 \cdot s)}] \qquad \textbf{(R5)}$$

The limiting reagent (LR) is the reagent that is used up first and, consequently, determines how much product can be obtained against the excess reagent (RE). Using the 1:1 stoichiometry between reactant-product of R1 and Avogadro's number to convert moles to molecules, the amount of OH$^-$ emitted can finally be expressed in terms of the limiting reactant:

$$\boldsymbol{c(OH\cdot)}\left[\frac{\boldsymbol{mol\grave{e}c}}{\boldsymbol{cm^3 \cdot s}}\right] = \boldsymbol{c^{RL}}\left[\frac{\boldsymbol{mol}}{\boldsymbol{cm^3 \cdot s}}\right] \cdot 6{,}022 \cdot 10^{23}\left[\frac{\boldsymbol{mol\grave{e}c}}{\boldsymbol{mol}}\right] \qquad \textbf{(R6)}$$

B. Study of the theoretical efficiency of the reaction

The theoretical efficiency of a reaction is defined as the capacity of the reaction to consume all the reactants as far as possible and at stoichiometric level, without taking into account the other external factors that occur in reality (additional evaporations, impurities...). Therefore, it will only depend on the deviation of the ratio between the reactants, with respect to the ideal stoichiometric ratio. c_i^{RE}, c_f^{RE}, represent the initial and final concentration, respectively, of the excess reagent, being the component with the highest concentration at the start of the reaction.

$$\boldsymbol{\eta_t} = \frac{\boldsymbol{c_i^{RE}} - \boldsymbol{c_f^{RE}}}{\boldsymbol{c_i^{RE}}} \cdot 100 \qquad \textbf{(R7)}$$

C. Analysis of reaction residues

According to the theoretical efficiency, the residues of the reaction (or final mixture), the final concentration of each reagent have been calculated in order to justify the regulation on the concentration of these reagents. Both values shall be expressed in ppm and an exposure time of 8 hours.

$$r(O_3) = (c(O_3) - c^{RL}) \cdot 8 \cdot 3600[s] \cdot 48\left[\frac{g}{mol}\right] \cdot 10^6\left[\frac{cm^3}{m^3}\right] \cdot \frac{1[m^3 O_3]}{2140[g]} \cdot \frac{1[ppm]}{1m^3/10^6 m^3} \quad \textbf{(R8)}$$

$$r(H_2O_2) = (c(H_2O_2) - c^{RL}) \cdot 8 \cdot 3600[s] \cdot 34\left[\frac{g}{mol}\right] \cdot 10^6\left[\frac{cm^3}{m^3}\right] \cdot \frac{1[m^3 H_2O_2]}{1386[g]} \cdot \frac{1[ppm]}{1m^3/10^6 m^3} \quad \textbf{(R9)}$$

2.3.2 Kinetic Study

In this section, the evolution over time of the concentration of hydroxyl radicals in a closed volume, starting from a concentration equal to the ambient concentration, will be estimated. Inside the enclosure area, one or more persons will be placed exhaling CO_2, without air renewal. This evolution will also be compared with an analogous case where there is also an external source of hydroxyl radicals by means of an OAF generating device. In any case, the various environmental chain reactions will be taken into consideration.

As a first approximation to the resolution of the time evolution of radicals in a closed and isolated volume, only those reactions involved in producing or eradicating radicals have been considered. These are those corresponding to carbon dioxide, hydrocarbons, bicarbonates, and carbon monoxide. It should be noted that the lifetime of OH· reactions with various volatile organic compounds is reduced in contrast to other reagents, such as O_3 and NO_3, justifying the effectiveness of OH· for the speed of pollutant eradication [27] [38] [39].

The **chain reactions** that generate or consume OH· cover the compounds shown in section 1.3, in particular in Figure 3, where the whole oxidation process provided by the OAF-generating device is schematized.

The following situations are identified:

- Volatile organic compounds react with radicals to generate carbon dioxide.
- Viruses and bacteria react with radicals to generate water.
- Various hydrocarbons can react with the radicals to generate carbon dioxide.
- Bicarbonates react with radicals to produce carbonates.
- Carbon monoxide can react with radicals to produce carbon dioxide.
- Oxygen reacts with radicals to produce ozone and water.
- Hydrogen peroxide reacts with radicals to produce ozone and water.
- Water reacts with radicals to produce hydrogen peroxide.

With all the reactions to be simulated exposed, the initial atmosphere of the closed control volume (of 300 m^3) is defined [40] [41] [42] [43].

First, equation R10 shows the initial or ambient concentration of hydroxyl radicals within the isolated volume of 300 m^3 (without air renewal), expressed in molec/cm^3.

$$[OH\,\cdot]: 10^7\,\frac{molec\ OH\,\cdot}{cm^3} \quad \textbf{(R10)}$$

Secondly, equation R11 shows the initial or ambient concentration of carbon dioxide inside the isolated volume of 300m^3 (without air renewal), expressed in ppm. Subsequently, this value is expressed in molec/cm^3 through the gas density.

$$[CO_2]: 412ppmCO_2 \cdot \frac{\frac{1m^3CO_2}{10^6m^3air}}{1[ppm_{CO_2}]} \cdot \frac{1{,}98kg}{1m^3} \cdot \frac{1000g}{1kg} \cdot \frac{1mol}{44g} \cdot \frac{1m^3}{10^6cm^3} \cdot \frac{6{,}022 \cdot 10^{23}molec}{1mol} \simeq 10^{16}\,\frac{molec\ CO_2}{cm^3} \quad \textbf{(R11)}$$

Thirdly, equation R12 shows the average initial or ambient hydrocarbon concentration inside the 300 m^3 isolated volume (without air renewal), expressed in ppb.

$$[Hidrocarbons]m: 26{,}9ppbHC \tag{R12}$$

Finally, equation R13 shows the initial or ambient concentration of carbon monoxide inside the isolated volume of 300m^3 (without air renewal), expressed in mg/m^3. Subsequently, this value is expressed in molec/cm^3.

$$[CO]: 0{,}115\frac{mgCO}{m^3}\cdot\frac{1g}{1000mg}\cdot\frac{1mol}{28g}\cdot\frac{1m^3}{10^6cm^3}\cdot\frac{6{,}022\cdot10^{23}molec}{1mol}\simeq 2{,}47\cdot10^{12}\frac{molec\ CO}{cm^3} \tag{R13}$$

The OH$^-$ emission rate by the OAF generating device is that corresponding to a purity of 4.95%:

$$\dot{X} = 2{,}84\cdot10^7\,\frac{molec}{cm^3\cdot s} \tag{R14}$$

On the other hand, the **lung capacity of a human** being will be taken into account in order to give magnitude to the exhaled volume of air, which partly includes a small portion of carbon dioxide. In concrete terms, the total capacity of a person is 4,6 liters of air, of which 1,6 liters is exhaled. The 4% of the exhaled volume represents the fraction of carbon dioxide that has been emitted by the individual. Taking into consideration that the human being multiplies the inhaled concentration of CO_2 approximately by 100, and considering the total volume of the room where he is, it will be possible to estimate the variation of carbon dioxide produced in the control volume, together with the chain reactions. Finally, an average of 16 exhalations per minute will be considered [44] [45] [46] [47].

Firstly, an indirect reaction between hydroxyl radicals and carbon dioxide can occur by the instantaneous uptake of an electron in a heavily NO_2^- polluted environment, such that carbonate ions are obtained from the reaction of carbon dioxide with hydroxyl ions [48] [49] [31].

$$OH\cdot + e^- \rightarrow OH^- \tag{R15}$$

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \tag{R16}$$

The combination of the above reactions gives the following overall expression:

$$2OH\cdot + CO_2 + 2e^- \rightarrow CO_3^{2-} + H_2O \tag{R17}$$

Thus, it should be noted that carbon dioxide represents the dominant reaction in the evolution of OH· over time. In fact, hydrocarbons and carbon monoxide react with radicals (separately) to produce the same carbon dioxide, and bicarbonates to produce carbonates. The higher the CO_2 concentration, the higher the consumption of radicals compared to the production of radicals in other reactions. The theoretical reactions of the above process are as follows:[50]

$$2\boldsymbol{OH}\cdot + \boldsymbol{CO}_2 + 2\boldsymbol{e}^- \rightarrow \boldsymbol{CO}_3^{2-} + \boldsymbol{H}_2\boldsymbol{O} \tag{R18}$$

$$\boldsymbol{HC} + a\boldsymbol{OH}\cdot \rightarrow b\boldsymbol{CO}_2 + \boldsymbol{H}\cdot \tag{R19}$$

$$\boldsymbol{HCO}_3^- + \boldsymbol{OH}\cdot \rightarrow \boldsymbol{CO}_3^-\cdot + \boldsymbol{H}_2\boldsymbol{O} \tag{R20}$$

$$\boldsymbol{CO} + \boldsymbol{OH}\cdot \rightarrow \boldsymbol{CO}_2 + \boldsymbol{H}\cdot \tag{R21}$$

The differential equations governing the kinetics of each reaction have been found to follow first and second order laws. In each expression the terms [X] indicate the concentration of the reactant or product X in molec·cm^{-3}, and the chemical kinetic constants of the reaction k in cm^3·molec^{-1}·s^{-1}. [51]

The different theoretical reactions are shown in (R18) through (R21). The corresponding differential equations governing the kinetics for each case are those shown in (R22) to (R25).

$$\frac{d[CO_2]}{dt} = -k_A[CO_2][OH\cdot]\ [52] \tag{R22}$$

$$\frac{d[HC]}{dt} = -k_B[HC][OH\cdot]\ [53] \tag{R23}$$

$$\frac{d[HCO_3^-]}{dt} = -k_C[OH\cdot][HCO_3^-]\ [54] \tag{R24}$$

$$\frac{d[OH\cdot]}{dt} = -k_D[OH\cdot]\ [55] \tag{R25}$$

With all this, we can obtain the global resolution of the system of differential equations that will allow us to calculate the [OH·] emitted (R26). The letters A-D refer to the different reactions considered (A corresponds to the variation of radicals referring to the reaction with carbon dioxide, B to hydrocarbons, C to bicarbonates and D to carbon monoxide). In addition, the character i refers to the assessment of the magnitude in the $i-ésimo$ instant of time, being $i=1$ the initial condition. The above expression is only valid in the absence of external OH· sources.

$$[OH\cdot]_{f,i} = [OH\cdot]_{f,i-1} + d[OH\cdot]_A + d[OH\cdot]_B + d[OH\cdot]_C + d[OH\cdot]_D \quad \textbf{(R26)}$$

In the case of inclusion of an OH· source, the [OH·] emitted shall be calculated according to R27, where $\dot{X}$ is the rate of radical emission produced by the OAF generating device.

$$[OH\cdot]_{w,i} = [OH\cdot]_{f,i} + Xdt \quad \textbf{(R27)}$$

Finally, it will also be necessary to define the numerical resolution of the rest of the compounds present in the air, since the infinitesimal variation of the OH· radical at an instant of time i will depend on the concentration of the other compounds at the same instant. For example, in the case of carbon dioxide:

$$[CO_2]_i = [CO_2]_{i-1} + d[CO_2]_A + d[CO_2]_B + d[CO_2]_D + d[CO_2]_{people,i} \quad \textbf{(R28)}$$

In this case, the reaction linked to bicarbonates does not contribute, as it neither consumes nor produces CO$_2$. Note that the additional term is included $d[CO_2]_{people,i}$, relating to the increase in carbon dioxide due to the exhalation of air by a group of people:

$$d[CO_2]_{people,i} = [CO_2]_i - [CO_2]_{i-1} = \frac{N_p[CO_2]_{i-1} f_a V_{ex}^{CO_2} + [CO_2]_{i-1}\left(V - V_{ex}^{CO_2}\right)}{V} - [CO_2]_{i-1} \quad \textbf{(R29)}$$

$$d[CO_2]_{people,i} = N_p[CO_2]_{i-1}\frac{(f_a-1)V_{ex}(p_c/100)}{V} = N_p[CO_2]_{i-1}\cdot 2{,}112\cdot 10^{-5} \quad \textbf{(R30)}$$

In the previous expression, N_p is the number of persons present inside the enclosed volume, f_a the amplifying factor of the carbon dioxide concentration produced by a human being (it is considered $f_a = 100$), V_{ex} the exhaled volume of air exhaled by a human being (it is considered $V_{ex} = 1{,}6L$), p_c the percentage of CO2 in the exhaled volume of air (according to WHO, $p_c = 4\%$) y V the volume of the enclosure area ($V = 300000L$).

Once the time distribution of the OH· has been obtained by evaluating the expressions from the instant $i=1$ to $i=i_{max}$, it is possible to obtain the rate of generation of these by means of the numerical derivative with respect to time. The instant $i = i_{max}$ is linked to the final instant of time $t=T$.

To meaningfully compare the difference between the case of 1 and 50 persons, the average increase in OH· concentration with the activated OAF generator device will be calculated. This is equivalent to the calculation of the area between the two curves on OH· radical emission with the activated and non-activated OAF generator device, weighted over time (numerical integral):

$$\Delta[OH\cdot] = \frac{1}{T}\int_0^T \left([OH\cdot]_w - [OH\cdot]_f\right)dt \quad \textbf{(R31)}$$

$$\Delta[OH\cdot] \simeq \frac{\Delta t}{2T}\sum_{i=1}^{n_t-1}\left([OH\cdot]_{w,i} + [OH\cdot]_{w,i+1} - [OH\cdot]_{f,i} - [OH]_{f,i+1}\right) \quad \textbf{(R32)}$$

2.4 Results of the Theoretical Model (Data Analysis)

2.4.1 Stoichiometric Study

The results deduced for the stoichiometric study are given below. These have been obtained using the expressions R3, R5, R6, R7, R8 and R9, given in the previous section, altering the 3 degrees of freedom: c (initial ozone concentration), p (purity of the 35 mL hydrogen peroxide solution), V (volume of the enclosed area where the reaction takes place). A fixed volume study was carried out on the one hand, and a fixed ozone concentration study on the other hand.

Firstly, the results according to the fixed volume model (OH· emission, theoretical efficiency, and residues) have been calculated for two magnitudes: 300 m^3 and 8 m^3. These values represent the room where the reaction would take place (once the reaction starts, the volume is considered constant).

For each volume value, the remaining two degrees of freedom have been iteratively altered: the concentration of ozone inside (in ppm) and the purity of the 35 mL tank of hydrogen peroxide (in %). In general, those combinations of both degrees of freedom that result in an efficiency close to 100% would imply minimization of reaction residues and maximum OH· emission.

A. Calculation of the [OH·] emitted according to the reagent concentration

Table 3 shows the concentration of hydroxyl radicals emitted for a fixed volume of 300 m^3 and 8 m^3 as a function of the alteration of the two remaining degrees of freedom: peroxide purity and initial ozone concentration. In general, it can be observed that the sensitivity of the emission to the change in peroxide purity or ozone concentration is always positive, until a constant emission value is reached. That is, if for example the evolution of the radical emission along a column of ozone concentration is analyzed, the radical emission would always increase with purity up to the point where ozone becomes the limiting reagent, where the radical emission would be constant for further changes in purity. The analysis would be completely analogous for each row of peroxide purity.

TABLE 3

Results of hydroxyl radical emission in the reaction of ozone with hydrogen peroxide (fixed volumes). Natural emissions measured according to absorption spectrum air-water/gas interface measurements report, spectroscopic signatures of ozone at air-water interface and photochemistry implications [56] – At cloudy day (air-water): $0,21 \cdot 10^{10}$ molecules per cm3 per second; at gas phase: $(0,7 - 10) \cdot 10^{6}$ molecules per cm3 per second.

		300 m^3					**8 m^3**				
$x10^6 \frac{molec\ OH.}{cm^3.s}$	**O_3**	**0,05 ppm**	**0,15 ppm**	**0,30 ppm**	**0,70 ppm**	**0,90 ppm**	**0,05 ppm**	**0,15 ppm**	**0,30 ppm**	**0,70 ppm**	**0,90 ppm**
H_2O_2											
0,25%		0,72	0,72	0,72	0,72	0,72	26,91	26,91	26,91	26,91	26,91
0,50%		1,43	1,43	1,43	1,43	1,43	43,56	53,81	53,81	53,81	53,81
0,75%		2,15	2,15	2,15	2,15	2,15	43,56	80,72	80,72	80,72	80,72
3,00%		8,61	8,61	8,61	8,61	8,61	43,56	130,69	261,37	322,87	322,87
4,95%		14,21	14,21	14,21	14,21	14,21	43,56	130,69	261,37	532,74	532,74
17,95%		43,56	51,52	51,52	51,52	51,52	43,56	130,69	261,37	609,87	784,11

The graph in **Figure 5** shows the evolution of the OH· radical emission for an ozone concentration of 0,05 ppm, as a function of the alteration of the two remaining degrees of freedom: the peroxide purity and the volume where the reaction takes place. It can be seen that the radical emission (per unit volume) is constant for small space enclosures, defining ozone as the limiting reagent.

However, as the volume where the reaction takes place increases, there comes a point where the specific radical emission starts to decrease, as hydrogen peroxide becomes the limiting reagent. The explanation for this decay rate lies in the fact that the peroxide reagent figure is given in absolute terms, as opposed to the ozone specification as a volumetric concentration, implying the generation of the same number of OH· molecules, but in an increasing volume.

Finally, as the peroxide purity increases, the onset of the specific emission drop is delayed in proportion to the magnitude of the increase in reacted H_2O_2.

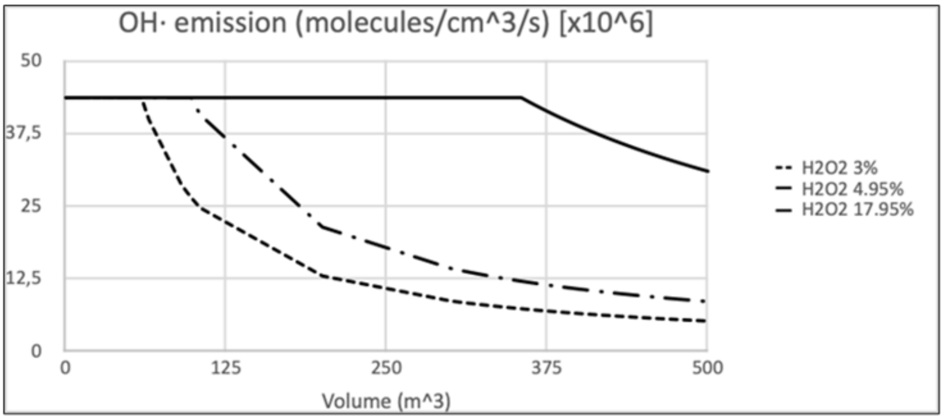

FIGURE 5: Results of the emission of hydroxyl radicals in the reaction of ozone with hydrogen peroxide using the previously justified formulation. Emission as a function of volume for different values of hydrogen peroxide purity and constant ozone concentration at 0,05 ppm (legal maximum for 8 hours)

On the other hand, it can be observed that for all volume values, there is always an emission of radicals of the order of 10^6 both measured and calculated [56].

B. Study of the theoretical efficiency of the reaction

Table 4 shows the theoretical efficiency of the reaction for a fixed volume of 300 m^3 and 8 m^3, depending on the alteration of the two remaining degrees of freedom: peroxide purity and initial ozone concentration. In line with the results of the radical emission, the maximum theoretical efficiency is obtained for those combinations of reagents that provide the maximum possible emission value, with the minimum residual of ozone and hydrogen peroxide.

Thus, a low efficiency value may imply that the radical emission is very low, and the presence of reagent residues is notorious. However, it is also possible that a low efficiency value is associated with a maximum emission, but not optimized by the large amount of residues present.

TABLE 4
THEORETICAL REACTION EFFICIENCY AS A FUNCTION OF VOLUME AND FOR DIFFERENT PURITY VALUES (FIXED VOLUMES).

		300 m^3					8 m^3				
%	O_3	0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm	0,05 ppm	0,15 ppm	0,30 ppm	0,70 ppm	0,90 ppm
H_2O_2											
0,25%		1,65	0,55	0,27	0,12	0,09	61,76	20,59	10,29	4,41	3,43
0,50%		3,29	1,10	0,55	0,24	0,18	80,95	41,18	20,59	8,82	6,86
0,75%		4,94	1,65	0,82	0,35	0,27	53,97	61,76	30,88	13,24	10,29
3,00%		8,61	6,59	3,29	1,41	1,10	13,49	40,48	80,95	52,94	41,38
4,95%		32,61	10,97	5,44	2,33	1,81	8,18	24,53	49,06	87,35	67,94
17,95%		84,56	39,42	19,71	8,45	6,57	2,25	6,76	13,52	31,57	40,59

The graph in **figure 6** shows the evolution of the theoretical efficiency of the reaction between ozone and hydrogen peroxide for an ozone concentration of 0,05 ppm, as a function of the alteration of the two remaining degrees of freedom: the purity of the peroxide and the volume where the reaction takes place. A maximum theoretical efficiency at a given volume can be observed in each curve. On the other hand, in the volumetric range where ozone is the limiting reagent (below the respective optimum volume) the efficiency starts to grow until it reaches 100% theoretical, when it then decreases, defining peroxide as the new limiting reagent. In this way, and linking the present graph with the previous one, an efficiency of 100% would indicate a maximum emission of OH·, while minimizing the final reaction mixture. For a volume lower than each optimum value

($V<V_{opt}$) the specific radical emission is still the maximum, but this is not optimized in terms of the amount of peroxide left over after the reaction.

Setting the ozone concentration value at 0,05 ppm (legal limit), it can be seen that a larger volume of the enclosure is required to obtain optimum efficiency as the purity of the hydrogen peroxide used increases. In other words, for each purity value there is an optimum volume where the reaction takes place. Likewise, the possible use of 17,95% peroxide is justified for enclosures with a large volume (around 350 m^3).

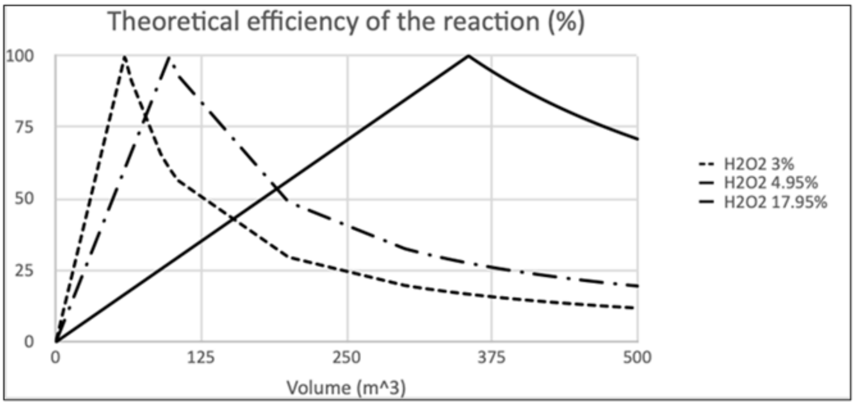

FIGURE 6: Results of the theoretical efficiency of the ozone reaction with hydrogen peroxide. Value as a function of volume for different values of hydrogen peroxide purity and constant ozone concentration at 0.05 ppm (legal maximum for 8 hours)

C. Residues analysis of the reaction

Table 5 shows the results for ozone and hydrogen peroxide residuals for a fixed volume of 300 m^3 and 8 m^3, expressed in ppm per 8h, as a function of the alteration of the two remaining degrees of freedom: peroxide purity and initial ozone concentration. Note how the highest efficiency values coincide with the respective lowest residual values. Also, the presence of residual defines which of the two reagents corresponds to the excess part, whose value depends on the extent to which the initial mixture of reagents departs from the ideal stoichiometric ratio.

It is important to identify which regions of the theoretical reaction efficiency are associated with ppm residues above a certain reference value, which could be the legal limit set by the competent bodies at international level.

TABLE 5
Results of the residues, or final mixture, in the reaction of ozone with hydrogen peroxide (fixed volumes). Ozone (O_3) emissions: Maximum emission recommended by WHO, OSHA, FDA of 0,05 ppm by volume. Hydrogen peroxide (H_2O_2) emissions: OSHA recommended maximum emission of 1 ppm (8 hour time-weighted average) [12] [57] [58].

		300 m^3					8 m^3				
%	**O_3**	**0,05 ppm**	**0,15 ppm**	**0,30 ppm**	**0,70 ppm**	**0,90 ppm**	**0,05 ppm**	**0,15 ppm**	**0,30 ppm**	**0,70 ppm**	**0,90 ppm**
H_2O_2											
0,25%		0,049 (O_3)	0,149 (O_3)	0,299 (O_3)	0,699 (O_3)	0,899 (O_3)	0,019 (O_3)	0,119 (O_3)	0,269 (O_3)	0,669 (O_3)	0,869 (O_3)
0,50%		0,048 (O_3)	0,148 (O_3)	0,298 (O_3)	0,698 (O_3)	0,898 (O_3)	0,012 (H_2O_2)	0,088 (O_3)	0,238 (O_3)	0,638 (O_3)	0,838 (O_3)
0,75%		0,048 (O_3)	0,148 (O_3)	0,298 (O_3)	0,698 (O_3)	0,898 (O_3)	0,044 (H_2O_2)	0,057 (O_3)	0,207 (O_3)	0,607 (O_3)	0,807 (O_3)
3,00%		0,040 (O_3)	0,140 (O_3)	0,290 (O_3)	0,690 (O_3)	0,890 (O_3)	0,327 (H_2O_2)	0,225 (H_2O_2)	0,072 (H_2O_2)	0,329 (O_3)	0,529 (O_3)
4,95%		0,034 (O_3)	0,134 (O_3)	0,284 (O_3)	0,684 (O_3)	0,884 (O_3)	0,573 (H_2O_2)	0,471 (H_2O_2)	0,318 (H_2O_2)	0,089 (O_3)	0,289 (O_3)
17,95%		0,009 (H_2O_2)	0,091 (O_3)	0,241 (O_3)	0,641 (O_3)	0,841 (O_3)	2,211 (H_2O_2)	2,109 (H_2O_2)	1,956 (H_2O_2)	1,548 (H_2O_2)	1,344 (H_2O_2)

For ozone, the maximum recommended emission for WHO, OSHA, FDA is 0,05 ppm by volume. For hydrogen peroxide, the maximum emission recommended by OSHA is 1 ppm by volume.

For this reason, and according to the regulations governing the maximum ppm for ozone and hydrogen peroxide, for large volumes (300 m^3) a hydrogen peroxide of 17,95% purity should be used, whereas for small volumes (8 m^3), a peroxide of 4,95% purity should be used.

The graphs in **Figure 7 and Figure 8** show the evolution of the residuals of the reaction between ozone and hydrogen peroxide, expressed in ppm per 8h, for an ozone concentration of 0,05 ppm and as a function of the alteration of the two remaining degrees of freedom: the purity of the peroxide and the volume where the reaction takes place. Linking these last two graphs with the previous ones, it can be seen how both residuals are zero at the optimum volumes corresponding to 100% efficiency, increasing as the volume of the room deviates from the optimum situation.

With regard to the reaction residues, starting from an initial ozone concentration equal to its maximum legal limit (0,05 ppm), this will never be exceeded. However, it should be noted that the hydrogen peroxide residues are lower than the legal limit of 1 ppm from a certain volume value for each purity. In other words, choosing a volume for the reaction lower than the minimum required value (corresponding to the 1 ppm residue) for a given purity value would imply non-compliance with the regulation.

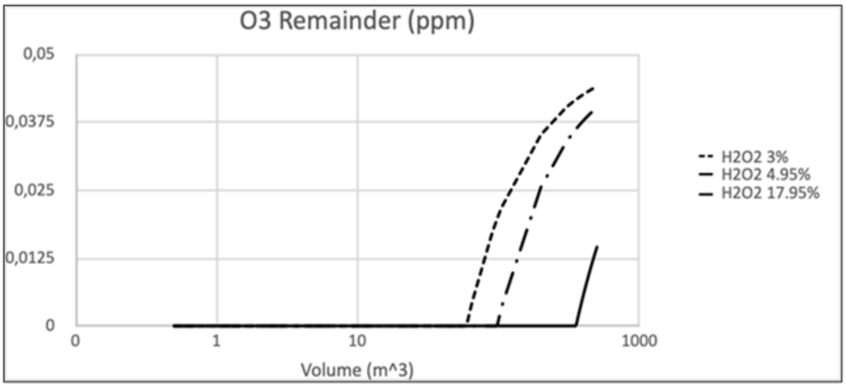

FIGURE 7: Ozone residues as a function of volume and for different purity values according to the results of the theoretical reaction efficiency. Ozone concentration constant at 0,05 ppm (legal maximum for 8 hours).

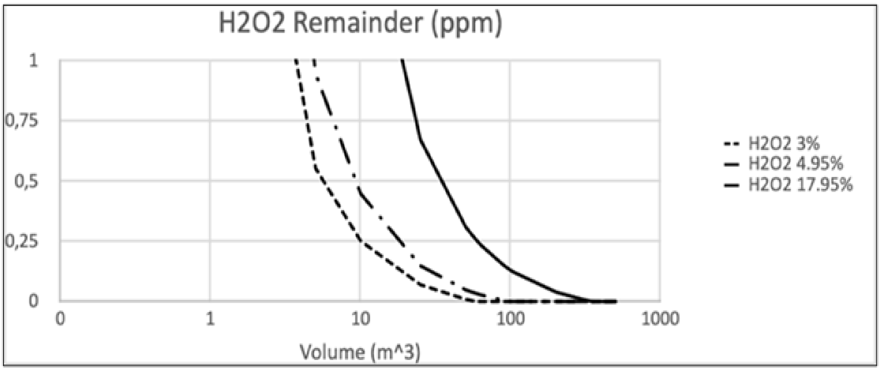

FIGURE 8: Residues of hydrogen peroxide as a function of volume and for different purity values according to the results of the theoretical reaction efficiency. Ozone concentration constant at 0,05 ppm (legal maximum for 8 hours).

2.5 Kinetic Study

The final results for the kinetic study are presented below. These have been obtained using the expressions R22-R32, presented in the previous section, and evaluated for all time instants. Specifically, the differential equations have been integrated for a time span of 30 minutes, considering the initial conditions of the concentrations of the environmental reagents indicated in R10-R13. First of all, the chemical kinetic constants of the various reagents involved are shown in the following table:

TABLE 6
RATE CONSTANTS FOR THE REACTION OF OH RADICALS WITH CONSIDERED REAGENTS [52] [53] [54].

Compound	Rate Constant $\cdot 10^{-12}$ [$cm^3/(molec \cdot s)$]
n-Butane	2.16E-12
n-Pentane	3.73E-12
n-Hexane	5.33E-12
n-Heptane	6.94E-12
n-Octane	8.84E-12
n-Nonane	11.8E-12
Benzene	1.08E-12
Toluene	5.69E-12
Carbon dioxide	9.77E-18
Bicarbonate ions	1.41E-14

This study is carried out for a single volume of 300 m^3 (without air renewal), during the 30 minutes of simulation and for two analogous cases with the presence of 1 or 50 people, as could be the case in an entertainment hall, in order to observe the impact of the exhalation of CO_2 from multiple people. For each of these two cases, the increase in radiative emission obtained by using the OAF generator device is compared with the case of natural evolution.

The graphs in **Figure 9** show the evolution of the hydroxyl radical concentration over time for 1 and 50 persons respectively. In addition, each graph compares the case with and without activation of the HFO generator device. The data have been obtained as a function of the initial concentration of the environmental reagents, integrating the system of differential equations and identifying the contribution for the case of OH·, as stated in R26 or R27. However, it should be noted that these expressions are dependent on the instantaneous concentration of the rest of the reagents, which will also be evaluated in each iteration of the time integration.

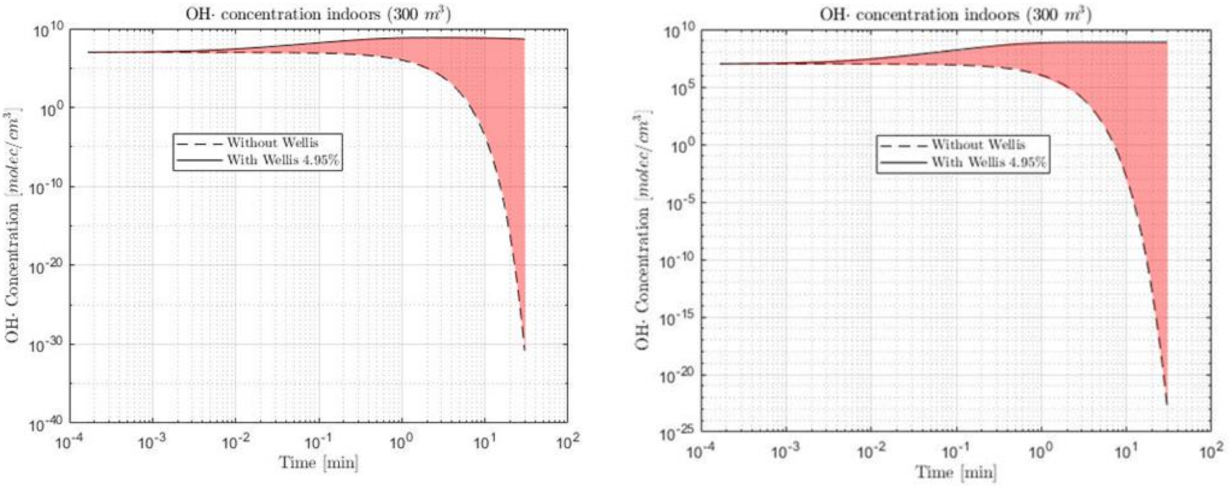

FIGURE 9: Time evolution of OH· in free air in the absence and presence of a source of radicals ("Wellis"), in the presence of 1 person (A) or 50 persons (B), taking into account an adult physiology in the frequency and value of carbon dioxide emission.

It can be observed that the concentration of radicals tends to zero in the absence of the device in both cases, 1 and 50 people, which is justifiable due to the lack of air renewal (the environmental reactions would end up consuming all the radicals). The incorporation of the OAF generating device helps to maintain (and even increase) the OH· concentration in this isolated enclosure without air renewal. In order to give magnitude to the difference between the 1 and 50 person case, and due to the similarity between the two graphs, the emission gain by the OAF generator device will be quantitatively estimated with respect to the no device case, for both the 1 and 50 person cases. Specifically, the post-processing expressions R31 and R32 above will be applied, using the previously calculated results, giving rise to the following values that indicate the average increase in emission obtained by activating the device:

$$\Delta[OH\cdot]_{N_p=1} = 7.372\cdot 10^8\,\frac{molec}{cm^3} \qquad \Delta[OH\cdot]_{N_p=50} = 5.911\cdot 10^8\,\frac{molec}{cm^3}$$

Note how the increase in emission for the 50 person case is lower than the emission corresponding to 1 person, thus indicating that a higher CO_2 exhalation implies a higher consumption of OH· radicals, as stated in the theoretical model. Finally, this effect can also be seen in **Figure 10**, where only the natural fall of OH· is compared between the cases of 1 and 50 persons, using the results already represented in the previous figure.

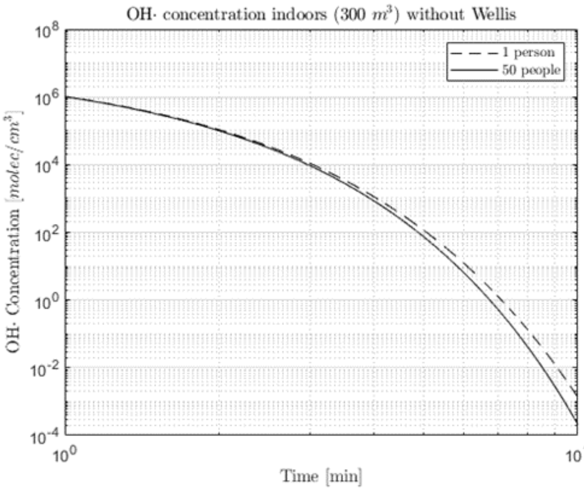

FIGURE 10: Time evolution of OH^- for 1 and 50 people, in the absence of a radicals source.

Again, in the 1 person case the concentration of OH· radicals are always higher than in the analogous 50 person case, as the exhalation of carbon dioxide is lower and consequently the fall of radicals is later. Quantitatively, the magnitude of difference between the 1 and 50 person cases is shown in the following table for the 1 and 10 minute times. Although initially the OH· decay is almost identical, at 10 minutes it is estimated that the radical emission with less CO_2 would be 6,3 times higher than the case with 50 people contributing to the exhalation.

TABLE 7
COMPARISON OF OH· EMISSION FOR 1 AND 50 PERSONS AT T=1MIN, T=10MIN.

	1 person	50 people	$r = 1p/50p$
$t = 1min$	$1{,}034\cdot10^6$ [molec/cm^3]	$1{,}017\cdot10^6$ [molec/cm^3]	1,017
$t = 10min$	$1{,}35\cdot10^{-3}$ [molec/cm^3]	$2{,}14\cdot10^{-4}$ [molec/cm^3]	6,308

III. DISCUSSION

Throughout this article, on the one hand, we have tried to answer the question posed at the beginning: What are the main atmospheric reactions involved in the formation of hydroxyl radicals from advanced oxidation processes and how do they evolve over time? With the results obtained, it has been possible to mathematically estimate that the outdoors concentration of OH·, which corresponds to its stationary or equilibrium concentration determined by the natural capacity of this species to transform into other species, is of the order of 10^6 molecules/cm^3 [15], [59]. The involvement of solar irradiation in the generation of OH· is noteworthy, as is the role of water in atmospheric chemistry, as clouds occupy 15% of the troposphere. The reaction rate in the aqueous phase is higher than in the gas phase (they occur earlier and faster), so each droplet acts as a small reactor where photochemically excited species are produced and generate radical species through energy transfer reactions, such as OH· [31]. For this reason, the atmospheric concentration of $OH^{\cdot}$ varies between 10^5 and 10^{10} molecules/cm^3 [56] and peaks of higher concentration are observed on very sunny days and on rainy days.

With the current information, it has been determined that the main source of OH^- outdoors, accounting for 70% of its generation, is ozone photolysis at wavelengths below 320 nm [40]. On the other hand, its indoors concentration is somewhat lower than outdoors, in the order of 10^5 molecules/cm^3, and its major source is the ozonolysis of alkenes, although the photolysis of nitrous acid (HONO) and formaldehyde (HCHO) is also relevant [20] [48]. Oxidation reactions between ozone and organic compounds (mainly terpenes present in perfumes and cleaning products), produce secondary non-volatile organic compounds in aerosols (SOA) even more dangerous than primary ones, such as formaldehyde [2] [8] [9] [31]. The accumulation of SOA and VOCs indoors is of strong concern due to their effect on human health, an accumulation that does not reach high concentrations in spaces where POA devices are safely used due to the constant promotion of oxidation [12] [20].

On the other hand, for the development of this article, different tests have been carried out, where different concentrations of hydrogen peroxide from 0,25% to 17,95% have been used, and it has been studied how it influences the reaction with 0,05ppm of ozone **(Maximum recommended emission by WHO, OSHA, FDA)**, both in a volume of 300 m^3 and in a volume of 8 m^3. Therefore, the complex reality of the chemical composition of our ambient air has been modelled as involving only two reactants: hydrogen peroxide and ozone, using a subsequent mathematical and analytical method for the final measurement of OH·. If you look at figure 6, you can see that for large volumes you would have to use 17,95% hydrogen peroxide as it does not exceed the maximum limit recommended by OSHA of 1 ppm hydrogen peroxide. On the other hand, for small volumes, it can be seen that 4,95% hydrogen peroxide would have to be used, as 17,95% would exceed the maximum permitted limit. In addition, it can also be seen in figure 5, the drop in the emission of hydroxyl radicals where, as the purity of the hydrogen peroxide increases, this drop is delayed.

Finally, with regard to the kinetic study, the general presence of hydrocarbons, carbon dioxide and HCO^{3-} ions have also been taken into consideration as factors to be taken into account in the rate of evolution of OH· concentration over time. Although a more realistic model has been chosen, it is still far from reality. In this case, the differential equations governing the kinetics of chemical reactions in the environment have been solved by numerical methods as an instantaneous measure of the OH· concentration. In general, the efficiency of the OAF generator device can be observed, since when this device is used, the hydroxyl radicals are maintained throughout the entire test.

Numerical techniques have been used as a method to measure OH·, given the defined model. Therefore, it is necessary to finish corroborating that the present model - preliminarily utopian - gives results consistent with other more realistic models and more experimental measurement methods.

In relation to the models of other studies, it is found that in general all authors conclude that the atmospheric sanitization is dominated by the participation of ozone and the subsequent production of OH· e.g. by hydrogen peroxide. However, some OH· degradation products do appear in some cases. For example, in one study the participation of other pesticides, such as chlordecone and beta-hex-achlorocyclohexane, is considered, and although they seem to show a much lower reactivity than ozone in the Fenton process, the component hydrochlordecone is obtained as a possible additional degradation product to be considered [60]. On the other hand, a promising UV/O_3 reactor was designed in another study for the degradation of Reactive Blue K-GL (RB), a dye used in the textile industry, and singlet oxygen concentrations are found as the primary species during mineralization, where OH· played an indispensable role [61]. However, in general the role of oxygen as a migratory agent in VOC mineralization processes at low temperature is fully confirmed [62]. Therefore, as a first iteration it is fully consistent to model the environment as the key involvement of ozone and hydrogen peroxide, having a suitable environment for the Fenton effect to occur. Also, in other studies it can be seen how with the help of a catalyst and VUV (vacuum ultraviolet) irradiation, it is possible to transform ozone into reactive oxygen species and OH·, improving the effectiveness in the mineralization of some VOCs [63]. Finally, a study shows how the kinetics of atmospheric oxidation of aniline (AN) initiated by OH· indicates that the dominant chain under atmospheric conditions is the inclusion of OH in one of the rings of AN [64].

In relation to the measurement techniques of other studies we can mainly find a widely used experimental method. The FAGE (Fluorescence Assay with Gas Expansion) technique is used in atmospheric studies, as it provides high sensitivity and selectivity for the species of the present study. In addition, the technique is relatively fast and non-destructive, which makes it suitable for real-time measurements in field situations. The technique is based on the property of certain chemical species to fluoresce when excited with ultraviolet (UV) light. The basic principle involves expanding an air sample through a region of ultraviolet laser light. The laser light is adjusted to a specific wavelength that matches the excitation of the molecules of the target species. When passing through the laser region, the molecules present in the sample are excited and emit fluorescence

[65]. In that study using FAGE, a concentration of $OH^{\cdot}$ in the absence of people of 5,9x10^5 molecules/cm^3 was obtained after 8 hours. Finally, another study uses rainfall collection for further analysis of the effect of microorganisms on the $OH^{\cdot}$ concentration of atmospheric water. Subsequently, the detection of OH^{-} is based on the reaction of ambient water with terephthalic acid (TA) and the product of TAOHs is quantified, given its strong fluorescence. Then, by means of chemical kinetics and stoichiometry, the $OH^{\cdot}$ concentration is calculated mathematically. We are therefore faced with another method, with a hybrid characterization between an experimental and a numerical part [66]. The results of the final $OH^{\cdot}$ concentration range from 2x10^4 molecules/cm3 to 1,20x10^6 molecules/cm^3, from the characterization of the sample as rain water to cloud water, respectively. Therefore, cloud water has a higher oxidative capacity and is more consistent with the present study, possibly due to the higher concentration of photochemical sources of $OH^{\cdot}$. In addition, hydrogen peroxide was found to be the major source of $OH^{\cdot}$ in the TA reaction. In conclusion, this method states that the model used in their study - and therefore in the present article - underestimates the source of the radicals, expecting an even higher $OH^{\cdot}$ emission in reality. Consequently, any advance in a more realistic model would enhance the results obtained, establishing our model and our measurement technique as a conservative and, even so, effective result given the characterization given to the OAF-generating device during the kinetic study.

IV. CONCLUSIONS

As it has been observed throughout this article, atmospheric air contains different volatile organic compounds, and it has also been shown that there are different reactants, radicals, anions and secondary compounds generated that intervene in the natural oxidation processes, but for this study only O_3 and H_2O_2 have been selected to analyze the reaction capacity to generate hydroxyl radicals ($OH\cdot$) and with an algebraic method a way to balance the stoichiometric redox type equations to measure the quantitative proportions or mass ratios of the chemical elements that are involved. These stoichiometric coefficients will indicate the proportion in which moles of reactants and products are involved in a chemical reaction.

In the stoichiometric study, a series of mathematical formulae were used to calculate both the efficiency of the reactions in % and the concentration of $OH\cdot$ from the purity of the hydrogen peroxide and the initial concentration of ozone, always in a safe way and without exceeding the emission limits established by the International Institutions. From this study and as has been mentioned in the discussions, it has been concluded that, for enclosures areas with large volumes, a peroxide of 17,95% will have to be used to achieve optimum efficiency of the $OH\cdot$ and a higher consumption of the two reactants. On the other hand, for enclosures areas with small volumes, a peroxide of 4,95% will have to be used.

On the other hand, in the kinetic study it has been possible to conclude that, simulating the main reagents present in the air, in a 30 minute simulation without the OAF generator device, after 1 minute, the natural hydroxyl radicals are practically non-existent. In contrast, when the OAF generator device is used, the hydroxyl radicals remain around 10^8molec/cm^3, a level that can be found directly in nature. Furthermore, by increasing the number of people in a room, the value of hydroxyl radicals will be lower due to the fact that the higher the concentration of CO_2 and other VOCs, the higher the consumption of these hydroxyl radicals due to a higher radical chain reaction.

To conclude, it has been demonstrated that in an artificial way and with the right combination, it is possible to reach the same value of hydroxyl radicals as in nature using the two reactant elements such as hydrogen peroxide and the almost negligible quantities of ozone, without exceeding **Maximum recommended emission by WHO, OSHA, FDA**.

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