GREEN CHEMISTRY: A PANACEA FOR ENVIRONMENTAL SUSTAINABILITY AGRICULTURE IN GLOBAL PERSPECTIVE

Dr E. A. Ubuoh
Department of Environmental Management Technology, Federal College of Land Resources Technology (FECOLART), Owerri, Imo State, Nigeria.

ABSTRACT: The environment is a very important component necessary for the existence of both man through agriculture. Agriculture is one of the oldest and global sources of human livelihood. Producing food, transportation, and energy for teeming population has led to large and widespread increases in the use of synthetic nitrogen (N) fertilizers and fossil fuel combustion, resulting in a leakage of N into the environment as various forms of air, soil and water pollution. Information for the paper was through secondary data, in which principles of green chemistry, impact of pesticides and inorganic fertilizers were discussed with the confirmation of negative impacts through their applications in agriculture. Sustainable Agricultural Applications in Green Chemistry was discussed and bio-pesticides and bio-fertilizers were recommended as an alternative tools. Green Chemistry aims not only for safer products, less hazardous consequences to the environment, saving energy and water, but includes broader issues which can promote in the end Sustainable Development. The beginning of green chemistry is frequently considered as a response to the need to reduce the damage of the environment by man-made materials and the processes used to produce them.

KEYWORDS: Green, Chemistry, Environment, Sustainability, Agriculture

INTRODUCTION

Agriculture is one of the oldest and global sources of human livelihood. It has matured from simple cultivation to sophisticated practices, and it is the second largest industrial contributor to global greenhouse gases (GHGs) [1]. It’s ahead of the entire transportation sector and behind only electrical and heat generation. During the last half-century, the use of chemical pesticides and fertilizers dominated agricultural practice and manufacturing industries rapidly expanded their use of synthetic chemicals in the production of consumer and industrial goods [2]. Agriculture releases to the atmosphere significant amounts of CO$_2$, CH$_4$, and N$_2$O [3]. According [4], the earth is only capable of absorbing 5 billion MT of CO$_2$ equivalents per year out of 5.6 billion MT of CO$_2$ that produced annually. According to[5], the scientific estimates of these gases indicate a rise in the global mean temperature. The increase in concentration of these gases could have far reaching consequences. Health effects from chemical emissions can be direct (occurring as an immediate effect of the emission) or indirect. Indirect health effects are caused by the emissions’ effects on water, air and food quality as well as the alterations in regional and global systems, such as red tide in many oceans, and the ozone layer and the climate, to which the emissions may contribute [6].

Over the past few years, the chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment. This new approach has received extensive attention and goes by many names including Green Chemistry, Environmentally Benign Chemistry, Clean Chemistry, Atom Economy and Benign by Design Chemistry. Under all of these different designations there is a movement toward pursuing
chemistry with the knowledge that the consequences of chemistry do not stop with the properties of the target molecule or the efficacy of a particular reagent. Much like the goal of "zero defects" that was espoused by the manufacturing sector, benign chemistry is merely a statement of aiming for perfection.

Green chemistry then can be defined as the design of chemicals, processes and reactions to reduce environmental and health hazards at source and to enhance sustainability, particularly through the molecular design of chemicals [7,8, ]. Green chemistry encompasses a range of scientific and technical developments aimed at ameliorating the chemical industry’s environmental and health impacts. The U.S. Environment Protection Agency defines Green Chemistry as an effort ‘to promote innovative chemical technologies that reduce or eliminate the use of generation of hazardous substances in the design, manufacture, and use of chemical products’ [ 9 ]. Many proponents have focused on toxicity reduction, namely making molecules less poisonous and using less toxic chemicals in manufacturing processes. The beginning of green chemistry is frequently considered as a response to the need to reduce the damage of the environment by man-made materials and the processes used to produce them. The definition of Green Chemistry and its Principles illustrates another important point about the use of the term “hazard”. This term is not restricted to physical hazards such as explosiveness, flammability, and corrosibility, but includes acute and chronic toxicity, carcinogenicity, environmental pollution to water, air and soil (aquatic organisms, mammals, etc) and ecological toxicity [10].

A quick view of green chemistry issues in the past decade demonstrates many methodologies that protect human health and the environment in an economically beneficial manner. This article presents selected examples of the implementation of green chemistry principles in agriculture for environmental sustainability.

**Principles of Green Chemistry**

In 1998, two US chemists - Paul Anastas, then of the United States Environmental Protection Agency, and John C. Warner developed 12 principles of green chemistry chemicals [10], which help to explain what the definition means in practice. The principles cover such concepts as:

(a) The design of processes to maximize the amount of raw material that ends up in the product;
(b) The use of safe, environment-benign substances, including solvents, whenever possible;
(c) The design of energy efficient processes;
(d) The best form of waste disposal: not to create it in the first place.

Green principles are needed to transform today’s environmental and technological disciplines and practices into ones that promote sustainability using the following twelve (12) green chemistry principles as summarized and contained in [10] as follow:

1. Prevent waste
2. Achieve atom economy: maximize incorporation
3. Use less hazardous synthesis steps
4. Design safer chemicals
5. Use safer solvents and auxiliaries
6. Design for energy efficiency
7. Use renewable feedstocks
8. Reduce derivatives
9. Catalytic reagents are superior to stoichiometric
10. Design for degradation
11. Real-time analysis for pollution prevention
12. Inherently safer chemistry prevents accidents

1.3 Concept of Environmental Sustainability:

[11] reported that “Environment” refers to the physical surroundings of man, of which he is part and on which he depends for his activities, like physiological functioning, production, and consumption. His physical environment stretches from air, water, and land to natural resources like metals, energy carriers, soil, and plants, animals, and ecosystems. In ecology the word describes how biological systems remain diverse and productive over times. For humans it is the potential for long-term maintenance of well-being, which in turn depends on the well-being of the natural world and the responsible use of natural resources [12], which is our focus today. Environmental sustainability is pursued with the idea of keeping the environment as pristine as naturally possible based on ideal-seeking behaviours (Chukwuma et al, 2012). Sustainability requires that human activity only uses nature’s resources at a rate at which they can be replenished naturally [13].

Environmental Impact of Pesticides used in Agriculture.

The term “pesticide” is a composite term that includes all chemicals that are used to kill or control pests. In agriculture, this includes herbicides (weeds), insecticides (insects), fungicides (fungi), nematocides (nematodes), and rodenticides (vertebrate poisons) [14]. Pesticides are recognized worldwide as a veritable means of controlling pests, at the same time such chemicals are highly toxic to other species in the environment [15;16;17]. Over 98% of sprayed insecticides and 95% herbicides reach a destination other than their target species, because they are sprayed or spread across entire agriculture field (Plate 1) [18] (George, 2004).

Adverse effects of chemical pesticides have been reported on both the abiotic and biotic components of the environment [19] The former are exemplified by residues in soil, air, water, food etc. and the latter by phytotoxicity, residues, vegetation changes etc. in plants and physiological deformities, diseases, mortality, population changes, genetic disorders etc. in mammals, avian, insects and other organisms [20]. Entry of pesticides into the food chain coupled with their bioaccumulation and biomagnifications trigger effects of unforeseen consequences. Chemicals like methyl bromide, chlorofluorocarbons etc. are established culprits for depletion of the ozone layer. To escape from these harmful effects, the concept of organic farming was emerged from the conference of Atlanta in 1981[20],

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Plate 1: Pesticide pathways: The Effect of Pesticides Application on Agriculture, Adapted from [12].

Human health effects are caused by: skin contact through handling, inhalation through breathing and ingestion through drinking contaminated food or in water by farm workers during farming activities [12].

The short-term (or acute) effects vary depending on the chemical, the dose received and the susceptibility of the individual exposed. These include burning, stinging or itching of eyes, nose, throat and skin. Other acute symptoms may include nausea, vomiting, diarrhea, wheezing, coughing and headache [21]. Although not all studies are consistent, several studies of women who work with pesticides suggest that some pesticides are associated with fertility problems and increased risks of spontaneous abortion and miscarriage [22].

Environmental Implications of Inorganic fertilizers in agricultural practices

In the last 50 years, synthetic fertilizer production, widespread cultivation of leguminous crops, and a variety of industrial processes including fossil fuel use have greatly increased the release of reactive nitrogen (Nr) to the environment [23]. Globally, the N cycle is perhaps the most altered of the major biogeochemical cycles, with serious implications for human health, biodiversity, air and water quality [23;24]. Fertilizers typically provide, in varying proportions: macronutrients: Nitrogen (N), Phosphorus (P), Potassium (K), Calcium (Ca), Magnesium (Mg), and Sulfur (S); and micronutrients: Boron (B), Chlorine (Cl), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), and Zinc (Zn). While the gains have been very impressive, the input intensive agriculture has resulted in some undesirable effects on the environment and the overall sustainability of the farming systems [25].

A major contributor of GHGs produced from modern agriculture is nitrous oxide (N₂O). Agriculture accounts for 84% of global N₂O emissions annually [26]. Typically, only 30% to 50% of nitrogen fertilizer applied to crops is absorbed by the crops. A significant portion of the unabsorbed nitrogen fertilizer volatilizes in the form of N₂O [27], through indiscriminate use of fertilizers, particularly the nitrogenous, which has led to substantial pollution of soil, air and water. Fertilizer contamination of ground waters has led to eutrophication of lake and river waters causing depletion of oxygen and even death of aquatic life through nitrate pollution. The presence of nitrates in potable water has been blamed for health hazards such as birth
defects, impaired nervous system, cancer and methaemoglobinemia (the blue baby syndrome) [28; 29]. Nitrogen fertilizers are predominantly urea (NH₂CONH₂). The advantage is that it is absorbed easily form the plants, but also it evaporates easily and can loose ~30% of its nitrogen to the atmosphere causing global warming[14]..

**Ecological effects of pesticides used in Agriculture**

The principal pathway that causes ecological impacts is that of water contaminated by pesticide runoff. The two principal mechanisms are **bioconcentration or bioaccumulation**: This is the movement of a chemical from the surrounding medium into an organism. The primary "sink" for some pesticides is fatty tissue ("lipids"). Some pesticides, such as DDT, are "lipophilic", meaning that they are soluble in, and accumulate in, fatty tissue such as edible fish tissue and human fatty tissue. Other pesticides such as glyphosate are metabolized and excreted) and **biomagnifications**: This term describes the increasing concentration of a chemical as food energy is transformed within the food chain. As smaller organisms are eaten by larger organisms, the concentration of pesticides and other chemicals are increasingly magnified in tissue and other organs. Very high concentrations can be observed in top predators, including man [29] ) catch in some wild fisheries, come from illegal, unreported and unregulated (IUU) fishing. Within the last two decades, there has been increasing awareness and concern among environmentalists regarding the effect of agrochemicals (Gammaline 20) on the status of aquatic health, particularly living resources like fish. The public health implications of eating fish contaminated with poisonous chemicals and heavy metals is worrisome, especially after the well-known Minamata Bay mercury pollution incident [30].

Above all, unsustainable fishing methods, such as : Dynamite fishing, electro-fishing, or fishing with poisons (Gammalin 20 -an organochlorine pesticide)) are, used in developing countries for fishing[31] . Application of Gammalin 20 was in fishing at higher concentrations observed the colour of the exposed fish becoming darker, opercular movement slowed down while pigmentation pattern increased and respiratory distress was observed, erratic swimming, tonic convulsion and no response to gentle prodding, and finally death [32] . The findings were consistent with the findings of authors like [33;34].

**Sustainable Agricultural Applications in Green Chemistry (Green Chemistry and Sustainable Agriculture).**

According to [35], sustainable agriculture seeks to achieve three goals: farm profitability; community prosperity; and environmental stewardship. The latter includes: protecting and improving soil quality, reducing dependence on non-renewable resources, such as fuel, synthetic fertilizers and pesticides and minimizing adverse impacts on safety, wildlife, water quality, and other environmental resources[36]. The use of toxic chemicals is clearly a destructive and dead-end approach to farming. Fortunately there are many alternatives to chemical farming. They go by the name bio-dynamic agriculture, permaculture, biological agriculture, organic farming, natural farming, indigenous farming systems, and ecological agriculture[35]. Biopesticides as organic factor are employed in agricultural use for the purposes of insect control, disease control, weed control, nematode control, and plant physiology and productivity[37]. Globally, during the past five years, biopesticide market has grown by nearly 10% per year, from more than $670 million in 2005 to $1 billion in 2010 [38]. Presently, biopesticides represent 2-6% of the approximately $40 billion global pesticide market. That share is expected to increase significantly through 2015 and beyond [13], due to its environmental friendliness in applications. According to [39]With an increasing
awareness about the harmful effects of synthetic plant protection and production agrochemicals, the demand for technologies and products based on biological processes has been increasing steadily worldwide.

**BIOPESTICIDES**

EPA recognizes three major classes of biopesticides: microbial pesticides, biochemical pesticides, and plant incorporated protectants [39].

1. **Microbial Biopesticides**: Microbial pesticides are products derived from various microorganisms (e.g., bacterium, fungus, virus or protozoan) that are used as an active ingredient to control pests. Microbial biopesticides are generally divided into six subcategories: *Bacteria, Viruses, Fungi, Protozoa, Yeast, and Nematodes*.

2. **Biochemical Biopesticides** are naturally occurring compounds or synthetically derived compounds that are structurally similar (and functionally identical) to their naturally occurring counterparts, which are characterized by a non-toxic mode of action that may affect the growth and development of a pest, its ability to reproduce, or pest ecology. They also may have an impact on the growth and development of treated plants including their post-harvest physiology. Biochemical biopesticides are generally divided into six subcategories: *Plant Growth Regulators (PGRs), Insect Growth Regulators (IGRs), Organic Acids, Plant Extracts, Pheromones and Minerals*.

3. **Plant-Incorporated Protectants**, also known as genetically modified crops, are pesticidal substances that plants produce from genetic material that has been added to the plant, such as corn and cotton. As defined by the United States Environmental Protection Agency (USEPA), biopesticides are certain types of pesticides, comprising living organisms or natural products derived from them are exemplified by plants (ex. pyrethrum *Chrysanthemum* sp., neem *Azadirachta* or *Melia* sp. etc.), *macrobiols* (ex. *Trichogramma* parasitoid-a *protozoan*, *Cryptolaemus montrouzieri*- a coccinellid predator etc.), microscopic animals (ex. *nematodes*), microorganisms including bacteria (ex. *Bacillus thuringiensis*), *viruses* (ex. nucleopolyhedrosis virus), *fungi* (ex. *Beauveria* sp.) and the *transgenic* plants containing a pest combating gene (ex. Bt cotton). Their key advantages include safety to mammals and other non-target organisms, environment compatibility, target specificity, lower exposure to pests, supplemental role to chemical pesticides enabling their use in integrated pest management and acceptability for use in organic agriculture [39]. Biofertilizers, or bioinoculants comprise environment friendly microorganisms which are beneficial to agriculture to improve soil fertility or crop productivity. They supply nutrients (ex. nitrogen) as well as improve availability of the unavailable forms of certain others (ex. phosphorus) and are comprised by several bacteria, fungi, actinomycetes etc. *Rhizobia, Azotobacter, Azospirillum*, blue green algae, *Azolla* and phosphate solubilizers (several bacteria and fungi) are the key examples. Their role in supplementing nutrition makes them ideally suitable in integrated nutrient management systems. A conventional idea of a sustainable fishery is that it is one that is harvested at a sustainable rate, where the fish population does not decline over time because of fishing practices. Sustainability in fisheries combines theoretical disciplines, such as the population dynamics of fisheries, with practical strategies, such as avoiding overfishing through techniques such as individual fishing quotas, curtailing destructive and illegal fishing practices by lobbying for appropriate law and policy, setting up protected areas, restoring
collapsed fisheries, incorporating all externalities involved in harvesting marine ecosystems into fishery economics, educating stakeholders and the wider public, and developing independent certification programs.

SUMMARY AND CONCLUSION

The environmental costs of agriculture, such as the deteriorating of atmospheric chemistry resulting to climate change, degradation of surface and underground water quality systems that affect man and his environment and pollution of soil that impacted food security negatively due to the application of chemicals to boast agriculture. Based on these, green chemistry which is more environmentally friendly technologies used for agricultural practices, if harnessed properly will pave way for sustainable agriculture.

Therefore, Green chemistry and sustainable agriculture are inherently intertwined; farmers need green chemists to make safe agricultural chemical inputs. Green chemists need farmers practicing sustainable agriculture to provide truly “green” It is therefore recommended that stakeholders in education, industries and environmental protection agency take a look at this proposal for implementation. There is a long term benefit of achieving sustainable environment devoid of prevalent environmental problems occasioned by incessant climate change and other greenhouse effects. Also, the success of green chemistry depends on the training and education of a new generation of Chemists/ Environmental Scientists, Students at all levels have to be involved in the philosophy and practice of green chemistry. The biggest challenge of green chemistry is to use its rules in practice.

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