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Life Cycle Assessment of Methyl Bromide Production and Utilization: Cradle to Grave Analysis

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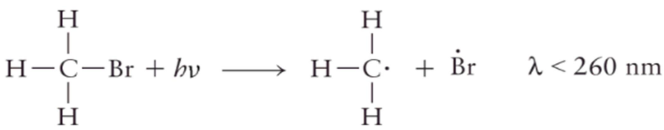
ABSTRACT

Methyl bromide is an effective and useful insecticide. It has ability to enter rapidly into materials at room temperature and pressure. Nowadays, it is primarily used for container fumigation purposes. However, exposure to it causes serious health-related issues. It is also one of the ozone-depleting substances. In this work, “cradle to gate” and “cradle to grave” approaches are considered to carry out a life cycle assessment of methyl bromide production. Sima Pro software with the IMPACT 2002+ method is used to compute the results. From the results of cradle to gate approach, it is inferred that major emissions are due to usage of plant utilities and methanol production process which have a substantial effect on the atmosphere. From the results of cradle to grave approach, it is noted that application of methyl bromide causes significant environmental damage particularly to ozone layer followed by non-carcinogen.

Keywords: Cradle to gate, Cradle to grave, Environmental impacts, Life cycle assessment, Methyl bromide.

INTRODUCTION

Methyl Bromide (MB) is a fumigant primarily applied to control weeds, pathogens, pests, nematodes, and rodents [1]. Previously the principal use of MB was for the fumigation of the agricultural soil and storage areas susceptible to pests [2, 3]. The application of MB (gas at temperatures above 4°C) as a soil fumigant results in almost complete eradication of populations of a wide variety of micro flora and fauna, as well as other soil organisms [4]. It has been studied that MB predominantly effects on ozone layer depletion [5, 6]. The amount of MB produced has been regulated because of its potential to cause ozone layer depletion. Countries such as the United States have completely phased it out since 2005 in compliance with the montreal protocol on constituents that result in Ozone Layer Depletion (OLD) and also under the Clean Air Act (CAA) [7]. However, MB is presently used under tight controls especially for container fumigation purposes. Its density is 3 times higher than air due to which it settles down in areas having low ventilation [8]. However, MB is approved fumigant for wooden packaging materials or pallets [9]. The total global production of MB was 13553 tonnes in 2017 including the 3,093 tonnes for laboratory and analytical uses (United Nations Environment Programme 2018) [10]. Some researchers have found out that MB is harmful since it causes site destruction in cells of an organism [11,12]. Researchers in their study have found evidence that MB causes genetic changes [13]. The U.S EPA classifies MB as a group D carcinogen as there is no adequate data for humans and animals which determines whether it causes cancer [14]. Generally, the atmospheric concentration of MB is approximately <0.025 ppb and in industrial areas, it is around 1.2 ppb. If proper personal protective types of equipment are not used, workers who are in direct contact with MB can be affected by high levels of MB. MB is naturally produced by algae or kelp in oceans [15]. The probability of groundwater contamination is very less as MB gets dispersed in the atmosphere during its application, however, the presence of MB have been noticed in drinking water MB is highly toxic [16]. It affects the lungs and neurological system in humans the typical symptoms of MB inhalation are dizziness, headache, convulsions, and difficulty in breathing, speech impairment, and body in-coordination. When exposed to skin it can result in itching and tingling while on being absorbed by the skin redness, pain and burning sensation with blisters can occur. Exposure to the eyes can result in blurred vision and temporary loss of sight. It is also classified as an endocrine-disrupting agent [17-23] biogenically in the ocean and emitted as soil fumigant (Reaction 1).



…………(1)

Once the atomic bromine is released, bromine catalytic ozone destruction gets started as shown in Reaction 2.

$$\dot{Br} + O_3 \longrightarrow Br\dot{O} + O_2$$
$$Br\dot{O} + \dot{O}\cdot \longrightarrow \dot{Br} + O_2$$
$$\dot{O}\cdot + O_3 \longrightarrow 2O_2 \quad \text{(net process)}$$

………… (2)

LITERATURE REVIEW

Micro-organisms and water also break down MB [24, 25]. From the above discussion, it is clear that the evaluation of environmental effects related to the production process of MB is required. This will help in planning to minimize these effects by way of source reduction and control. Life Cycle Assessment (LCA) is a tool to estimate the environmental impacts associated with any service/product or process over its entire life cycle right from the extraction of the raw material to its use and finally its eventual disposal [26].

There are no research details available on the LCA study of the production process of MB. However, the environmental impact associated with the application of MB as a fumigant has been compared with other pest treatment methods wooden pallets including conventional Heat Treatment (HT), and Micro wave induced heat treatment [7]. The results of this study revealed that among the three treatment methods, MB has a greater impact on Global Warming (GW) and OLD. However, the detailed environmental impact assessment for the MB production process is necessary. In this work environmental impacts associated with the production of MB have been estimated using LCA.

Methyl bromide process description

There are for main stages to produce MB

- Reaction
- Purification
- Condensation
- Storage and packaging

Reaction: The raw materials required for the reaction are methanol, hydrogen bromide and sulphuric acid in which methanol converts into MB (Reaction 3).

$$CH_3OH + H_3O^+ + Br^- \xrightarrow{\text{conc.sulphuric acid}} CH_3Br + 2H_2O \cdots(3)$$

The reactor should be cooled since the reaction is exothermic. Hydrogen bromide supply is controlled by bromine by the reaction of bromine and sulphur as shown below Reaction 5.

$$3Br_2 + \frac{1}{8}S_8 + 11H_2O \rightarrow 7H_3O^+ + 6Br^- + HSO_4^- \cdots(4)$$

The by-product of this reaction is sulphuric acid. The reactants do not get converted and by-products are also formed. Hence MB needs to be purified.

Purification: The crude MB is purified by various steps like washings, distillations, and extractions. After the treatment, hydrogen bromide and bromine traces are removed but also generate water vapours. To remove this water and dry the product, sulphuric acid is used. The sulphuric acid is then transferred to the distillation tower. The un-reacted reactants are recycled to the reactor and MB and sulphuric acid are obtained as product and by-product respectively (Reactions 5 and 6).

.

$$HBr + OH^- \rightarrow Br^- + H_2O \cdots\cdots\cdots\cdots (5)$$

$$3Br_2 + 6OH^- \rightarrow 5Br^- + BrO_3^- + 3H_2O \cdots\cdots\cdots\cdots(6)$$

Condensation: The pure MB obtained from the purification is then condensed and stored. Condensation takes place into two steps. First it is cooled with a brine solution to -20 ºC and then by ammonia to -40 ºC. Hence MB gas liquefies with very low vapour pressure. To trap the uncondensed gas, a deep cooling system with an absorption column is attached. It prevents the gas from any leakage.

Storage and packaging: Condensed MB is stored in double-walled storage tanks. Before shipping, it is kept in ISO tanks and containers which can resist the pressure of 15 atm but to be on the safer side it is filled at 6 atm pressure. Detailed data with regards to the raw materials, utility requirements, products, emissions, and effluent, has been provided by Intech Organics Ltd for this study.

Life cycle assessment

Nowadays, resource and environmental problems linked to industrial growth have become progressively more obvious. Many businesses have realized that it is imperative to look at ways of using various approaches for the reduction in pollution at the source and environmental management systems to improve their environmental performance. LCA is such a tool for quantifying the environmental impact along with the product entire life cycle. LCA is a scientific assessment technique to encourage resource-saving and environmental protecting behaviour and could provide a better understanding of potential environmental impact for the decision-making process [27].Therefore these days, LCA has become one of the most accepted and used tools for the environmental assessment of products and services [28]. This paper presents LCA study on MB production using a cradle-to-grave approach and results have been compared with cradle to gate approach so that environmental impacts due to the application of the product are also understood. This would help decision-makers in taking appropriate decisions regarding the preventive steps to reduce the overall impact of product development.

Life cycle assessment methodology

The LCA consists of four steps: goal definition and scoping, inventory analysis, impact assessment, and interpretation and are explained in the following section [29-37].

Goal and scope definition: The goal of this study was to estimate environmental impacts associated with the MB production facility located at Intech Organics Ltd(formerly known as Intech Pharma Pvt. Ltd), Dhargal Goa, India. Two approaches *viz.* Cradle to Gate (CTGT), and Cradle to Grave (CTGR) have been used to carry out LCA of MB production. The LCA system boundaries, for the MB production process, using CTGT and CTGR are presented in Figures 1a and 1b.

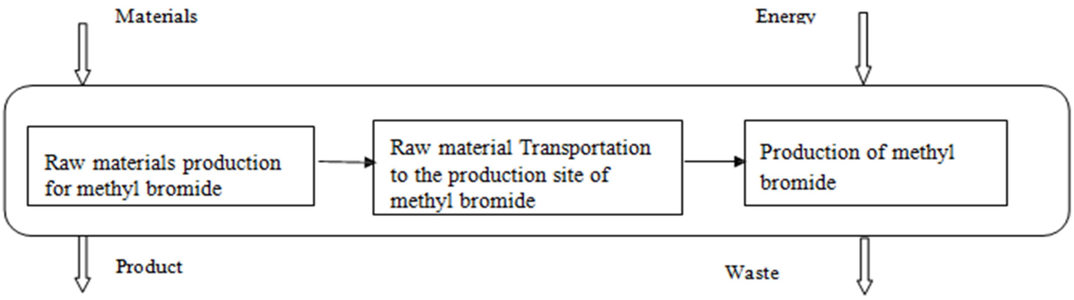


Figure 1(a): Stages in the life cycle of a methyl bromide production (LCA system boundary) for Cradle to Gate (CTGT) approach.

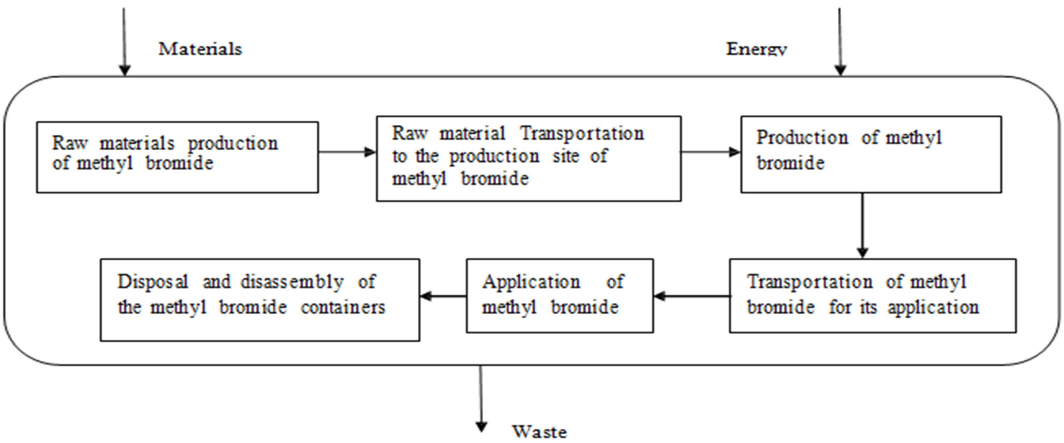


Figure 1(b): Stages in the life cycle of a methyl bromide production (LCA system boundary) for Cradle to Grave (CTGR) approach.

Functional unit: For this study functional unit of 1 kg, MB manufactured, packaged, transported, and used is considered.

Life cycle inventory analysis

The block diagram of the MB production process is shown in Figure 2. The reaction scheme is shown in Reaction 7.

$$6CH_3OH + 3Br_2 + S \rightarrow 6CH_3Br + H_2SO_4 + 2H_2O \cdots (7)$$

Inventory data for production of 1 kg of MB is given in Table 1. Table 1 also includes data for raw material transportation, energy requirements, product packaging materials, and emissions. Transport, application, emissions of MB, and disposal of materials used to contain MB are given in Figure 2 and Tables 1 and 2.

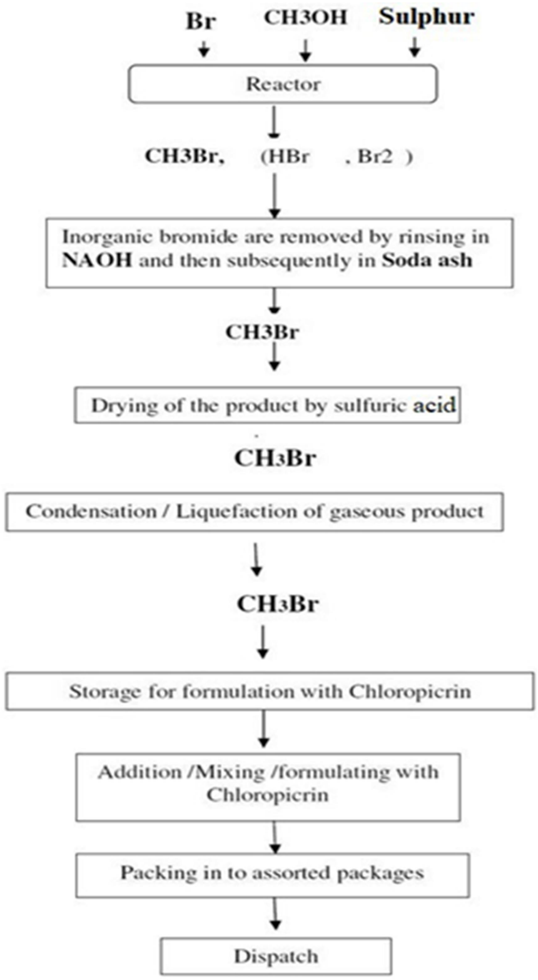


Figure 2: Block diagram for MB production.

Input/output material and energy	Quantity	Unit
Raw materials		
Methanol	0.387	kg
Bromine	0.672	kg
Sulphur	0.062	kg
Sulphuric acid	0.132	kg
Sodium carbonate	0.005	kg
Sodium hydroxide	0.005	kg
Water	0.1588	kg
Transport of raw materials		
Roadways: Diesel truck	500	kg km
Energy inputs		
Electricity	0.73	kwh
Steam	0.756	kg
High speed diesel	0.0254	kg
Emissions		
Particulate matter	0.077	g
Sulphur dioxide	0.311	g
Nitrogen oxides	0.006	g
Carbon monoxides	0.005	g
Hydrocarbons	0.006	g
COD	0.0156	mg
Suspended solids	0.012	mg
Oil and grease	0.008	mg
Packaging of MB		
Cylinders	0.36	kg
Cans	0.03	kg

Table 1: Inventory data for production of 1 kg of MB.

Input/output	Quantity	Unit
Transport of product		
Roadways: Diesel truck	500	kg km
Application		
MB	1	kg
Air emission		
MB	0.87	kg
Recycling of packaging material		
Steel and iron cylinder	0.36	kg
Aluminium can	0.03	kg

Table 2: Inventory data for transport, application, and emissions of MB during the application and disposal of materials used to keep MB.

Life cycle impact assessment: Life Cycle Impact Assessment (LCIA) is carried out using SimaPro software. For this study IMPACT, 2002+ method is considered. This method proposes a possible execution of a combined midpoint approach, connecting all types of life cycle inventory results *via* 15 midpoint categories to four damage categories (ILCD, 2010; Eco-indicator 99 and CML 2002). Normalization can be performed either at the midpoint or at damage level. For this study, normalization is performed at the midpoint level.

Cradle to gate approach

The LCA study of the MB production process is carried out using the CTGT approach. In this approach, raw materials production processes along with the production process of MB are considered. Transportation of raw materials and packaging of the product are also considered for the CTGT analysis. The LCA results, obtained using this approach, are presented through Figures 3 and 4. The characterization of emissions in the production process of MB is shown in Figure 3. From Figure 3 it is observed that the methanol production process, electricity use, diesel combustion, and onsite steam production have a significant environmental impact as compared to the MB production process. The various environmental attribute affected are also indicated in Figure 3. It is also observed that the production process of sulphur and the transportation of raw materials have a notable impact on various impact categories. However, the production process of MB has a minor impact on only respiratory inorganics, terrestrial and aquatic acidification, aquatic eutrophication, and global warming. From these results, it is revealed that the production of raw materials and energy causes significant environmental impact as compared to the production process of methyl bromide.

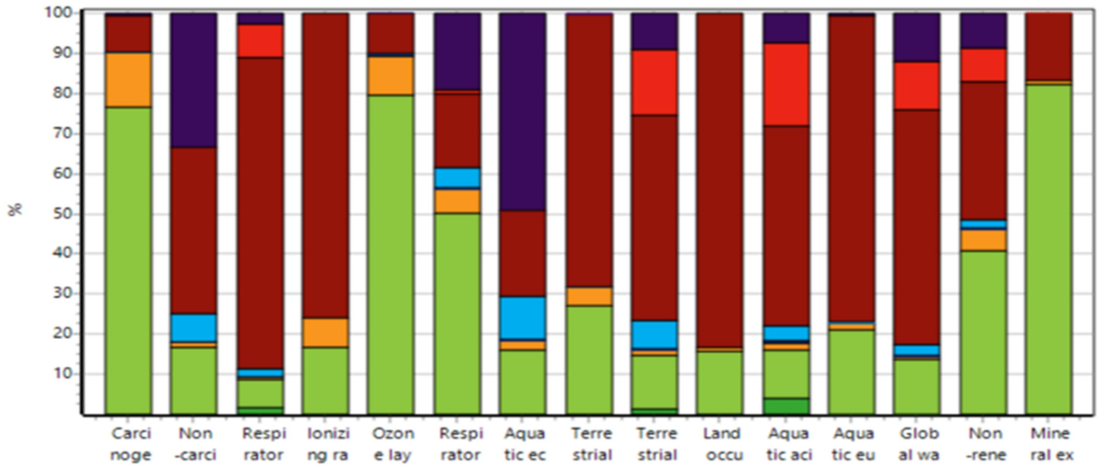


Figure 3: Characterization of emissions in MB production using the CTGT approach.

■ Methyl Bromide ■ Sodium hydroxide, production mix, at plant/RNA

■ Methanol (GLO) (market for) APOS, U ■ Transport combination truck, diesel powered/US

■ Sulphur (GLO) (market for) APOS, U ■ Electricity, high voltage (IN southern grid) (market for electricity, high voltage) Cut-

■ Dummy_ sodium carbonate/kg/RNA off, U

■ Diesel, combusted in industrial boiler/US ■ On-site steam average E

Method: IMPACT 2002+ V_2.14/IMPACT 2002+/Characterization Analysing 1 kg Methyl Bromide.

In the CTGT approach, normalization and single score analysis of impact assessment results in MB production are done and are presented in

Figures 4a and 4b. The reference factor for normalization is the total impact of all substances of the specific category for which characterization

factors exist, per person per year (for Europe). From Figure 4a it is seen that significant impact due to various activities during MB production is on respiratory inorganics, non-renewable energy, and global warming. In a single score, analysis calculations are made on endpoint categories. From Figure 4b it is observed that electricity usage and methanol production are primary processes that cause the impact on the above-said categories. It is to be noted that in this study, methanol production is from natural gas, which is called the greener route. Despite the use of greener route, the environmental impacts are more due to the methanol production process as compared to other processes. If methanol production is done using coal or coke oven gas, the environmental impacts will further increase. On-site steam production and diesel combustion in boilers also affect the said categories (Figures 4a and 4b).

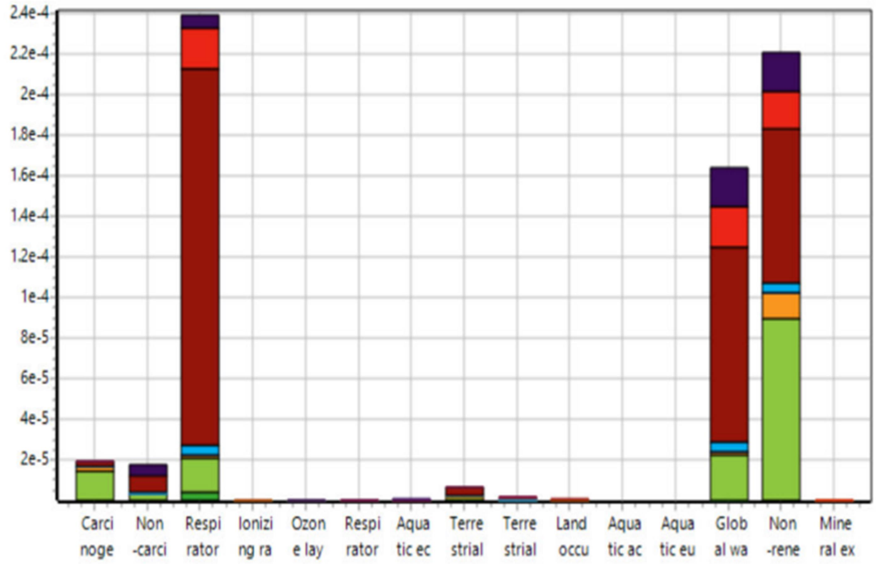


Figure 4(a): Normalization of impact assessment results of MB production in the CTGT approach.

- Methyl Bromide
- Sodium hydroxide, production mix, at plant/RNA
- Methanol (GLO) (market for) APOS, U
- Transport combination truck, diesel powered/US
- Sulphur (GLO) (market for) APOS, U
- Electricity, high voltage (IN southern grid) (market for electricity, high voltage) Cut-off, U
- Dummy_ sodium carbonate/kg/RNA
- Diesel, combusted in industrial boiler/US
- On-site steam average E

Method: IMPACT 2002+ V_2.14/IMPACT 2002+/Normalization Analysing 1 kg Methyl Bromide.

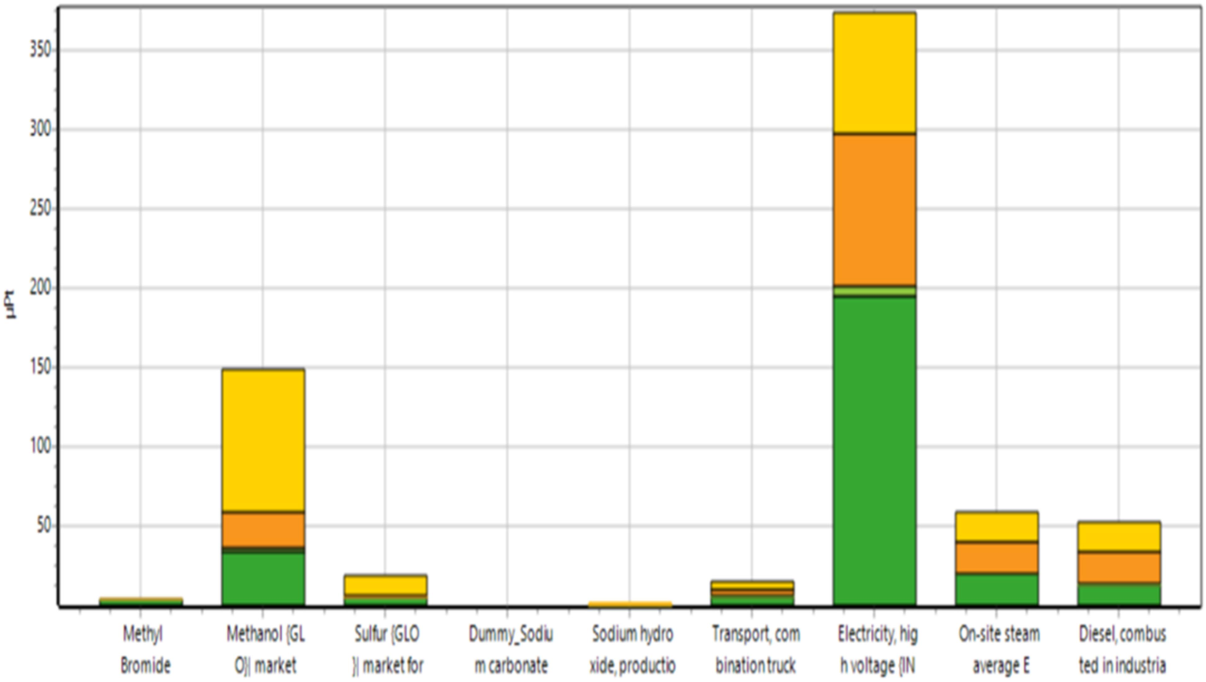


Figure 4(b): Single score analysis of emissions from MB production in the CTGT approach.

■ Human health ■ Climate change ■ Ecosystem quality ■ Resources

Method: IMPACT 2002+ V_2.14/IMPACT 2002+/Single score analysing 1 kg Methyl Bromide.

Cradle to grave approach

In the CTGR approach, all the stages in MB production starting from production processes of raw materials, transportation of raw materials, the onsite production process of MB, transportation of MB, application of MB, and recycle of containers used for handling of MB are considered. This approach is a combination of CTGT and gate to grave approaches. Transport of MB is considered through roadways by using diesel-powered trucks within India for 500 kg km per kg of MB. Post application, 87% of MB is considered to be emitted into the atmosphere in 7 days. Steel and aluminium containers used for storage of MB are considered to be recycled. The LCA results of MB using the CTGR approach are presented through Figures 5 and 6. Characterizations of emissions from the production process of MB using the CTGR approach are presented in Figure 5. From Figure 5 it can be noted that the application of MB impacts the ozone layer since, during the application, MB breaks into bromine ion which directly depletes the ozone layer *via* reactions 1 and 2 mentioned elsewhere in this article. Application of MB also affects impact categories such as non-carcinogens, terrestrial and aquatic ecotoxicity, and in global warming. Transportation of MB through roadways by diesel-powered trucks is having an insignificant effect on the environment as compared to other activities. However, recycling of steel cylinders and aluminium cans of MB helps in improving the environmental conditions by reducing emission (Figure 5).

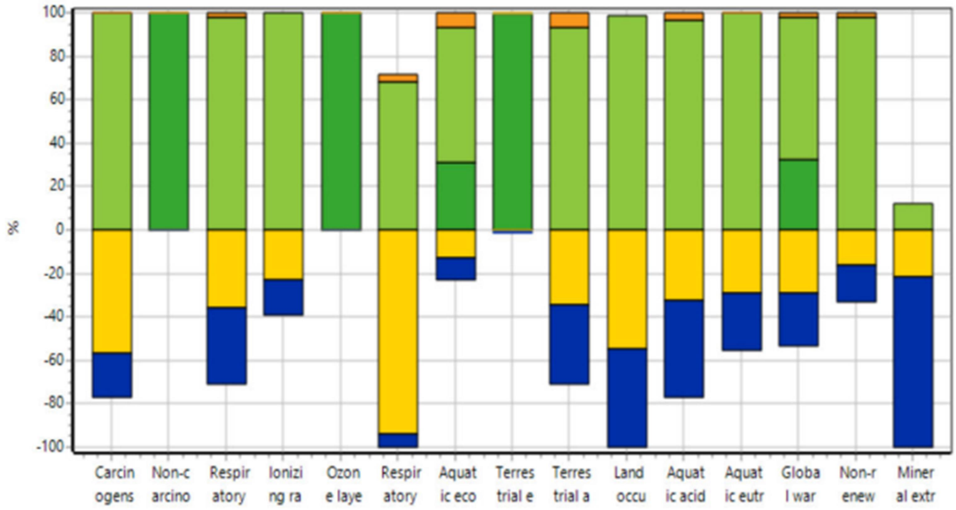


Figure 5: Characterization of emissions from MB production in the CTGR approach.

■ Methyl Bromide application ■ Transport combination truck, diesel powered/US ■ Methyl Bromide ■ Steel and iron (waste treatment) (GLO) recycling of steel and iron APOS, U ■ Aluminium (waste treatment) (GLO) recycling of aluminium APOS, U

Method: IMPACT 2002+ V_2.14/IMPACT 2002+/Characterization Analysing 1 kg Methyl Bromide.

Normalization and single score analysis of impact assessment results of MB using the CTGR approach are presented in Figures 6a and 6b. From Figure 6a, it is noted that among the impact categories affected due to MB production, the ozone layer is most the most affected impact category followed by non-carcinogen. This is primarily in the MB application stage as seen from Figure 6b. In the case of single score analysis, human health is significantly affected endpoint category (Figures 6a and 6b).

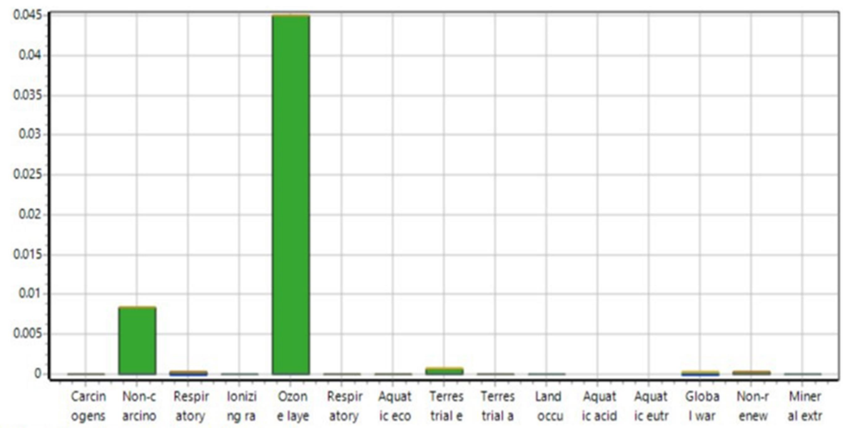


Figure 6(a): Normalization of impact assessment results of MB using the CTGR approach.

■ Methyl Bromide application ■ Transport combination truck, diesel powered/US ■ Methyl Bromide ■ Steel and iron (waste treatment) (GLO) recycling of steel and iron APOS, U ■ Aluminium (waste treatment) (GLO) recycling of aluminium APOS, U

Method: IMPACT 2002+ V_2.14/IMPACT 2002+/Normalization Analysing 1 kg Methyl Bromide.

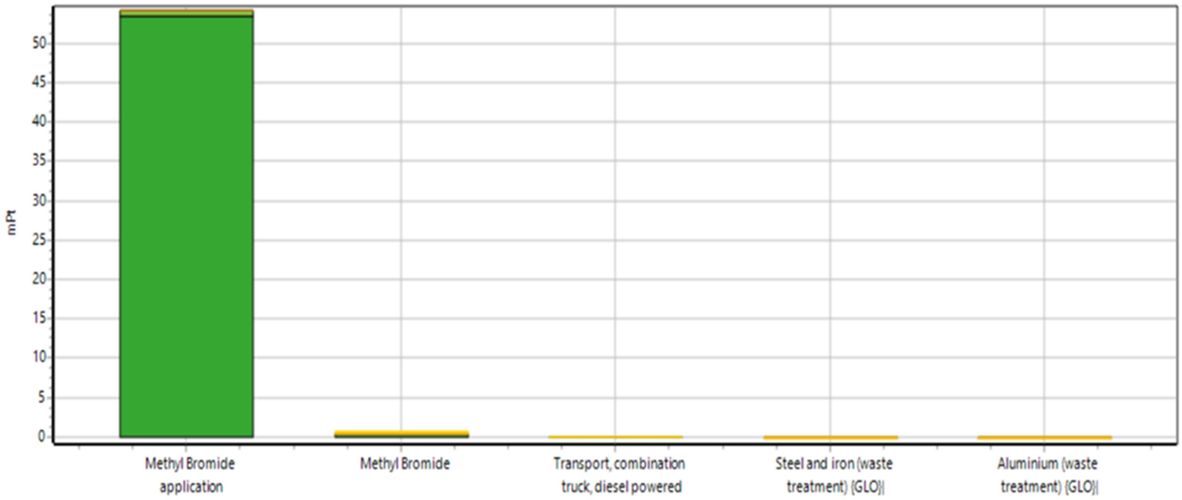


Figure 6(b): Single score analysis of impact assessment results of MB using the CTGR approach.

■ Human health ■ Climate change ■ Ecosystem quality ■ Resources

Method: IMPACT 2002+ V_2.14/IMPACT 2002+/Single score Analysing 1 kg Methyl Bromide application.

CONCLUSION

Assessment of environmental impacts associated with MB manufactured at Intech Organics Ltd, Dhargal, Pernem, and Goa, India is ascertained. Two approaches *viz.* CTGT and CTGR are considered for the said study. With an increase in the boundary of the process, the complexity of LCA analysis is also increased. With an increase in system boundary of LCA study, the contribution of various stages of MB's life cycle, in environmental impact are also varied.

From results and discussion of CTGT study, it is revealed that usage of the plant utilities and methanol production (one of the raw materials for production of MB) are primary processes which cause the notable impact on respiratory inorganics, non-renewable energy, and global warming compared to other stages in LCA of MB. It is important to note that in this study, methanol production is considered to be from natural gas, which is called the greener route. Despite this, the environmental impacts are more due to the methanol production process as compared to other processes. From results and discussion of CTGR study it is revealed with the expansion of system boundary, the stages in LCA of MB, which affect the environment, are also changed. Application of MB significantly impacts the ozone layer, since, during the application, MB breaks into bromine ion which directly depletes the ozone layer. However, recycling of steel cylinders and aluminium cans of MB helps in resource conservation and also a reduction in environmental impact.

The environmental impact due to onsite usage of plant utilities can be significantly reduced by substituting conventional fuels with environment-friendly fuels and the use of non-conventional energy. Because of significant negative impact on the environment during MB application, it is recommended that alternative fumigants such as phosphine, sulphuryl fluoride, carbonyl sulphide, ethyl formate, ozone, hydrogen cyanide, carbon disulphide, mono-terpenes from plants or non-chemical alternatives like irradiation along with atmosphere control using nitrogen and carbon dioxide, heat and cold can be used.

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