United States Department of Agriculture
Agricultural Marketing Service | National Organic Program
Document Cover Sheet
https://www.ams.usda.gov/rules-regulations/organic/petitioned-substances

Document Type:

☐ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

☒ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

Ethylene

Crops

Identification of Petitioned Substance

Chemical Names:
C_2H_4; acetene; elayl; ethene

Other Names:
bicarburreted hydrogen; ethylene gas; olefiant gas

Trade Names:
Ethylene; Fruit Ripening Ethylene; Banana Gas; Natur-Ripe; Color Ripe

CAS Numbers:
74-85-1

Other Codes:
UN II: 91GW059KN7
EPA: PC code 41901
EC number: 200-815-3

Summary of Petitioned Use

The United States Department of Agriculture (USDA) National Organic Program (NOP) included ethylene on National List of Allowed and Prohibited Substances (hereafter referred to as the National List) at 7 CFR 205.601(k) as originally published December 2000, for use to regulate flowering in pineapple (65 FR 80547). It was also listed for post-harvest handling to ripen tropical fruit at §205.605(b). In November of 2003, the NOP changed the annotation for the post-harvest allowance to also allow for degreening of citrus (68 FR 61987). This Crops technical report principally addresses the use of ethylene to regulate pineapple flowering, while the Handling technical report focuses on the post-harvest handling uses of ethylene for tropical fruit ripening and citrus degreening.

Characterization of Petitioned Substance

<u>Composition of the Substance:</u>

C_2H_4

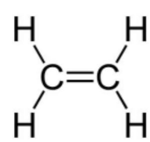

Figure 1. Structure of ethylene (CanHealth, 2016)

Ethylene is the simplest of the alkenes. Alkenes are defined as hydrocarbons with a carbon-carbon double bond (Bruice, 2001). Hydrogen atoms surround the two-carbon chain. The structure is analogous to ethane (C_2H_6), but with a double bond rather than a single bond and fewer hydrogen atoms (see **Figure 1**).

Ethylene is a colorless, flammable gas that is lighter than air and has a sweet odor and taste (NCBI, 2022a). When ignited, it can quickly burn back to the source of the leak. It can be shipped as a gas in canisters, or as a refrigerated, pressurized liquid (cryogenic liquid) which must be shipped below 50°F (10°C). Fruit producers and handlers sometimes make ethylene on site, converting ethanol with a catalytic generator (see *Evaluation Question* #2). Vapors arising from the boiling liquid are lighter than air (NCBI, 2022a). It is non-toxic, but it is an asphyxiant (NCBI, 2022a). Under prolonged exposure to fire or intense heat, containers of ethylene may rupture violently and rocket (NCBI, 2022a).

Synthetic ethylene gas used in crop production is chemically identical to the natural form produced by plants (Abeles, 1992; Bartholomew, 2014).

Source or Origin of the Substance:

Most ethylene gas manufactured globally is made as a pyrolysis product of petroleum hydrocarbon feedstocks, such as natural gas liquids or crude oil (NCBI, 2022a; Zimmerman & Waltz, 2011). Ethylene gas can also be produced in small quantities in on-site fruit ripening facilities by catalytic generators from ethanol (Zimmerman & Waltz, 2011; NW Hort. Council, 2008).

Properties of the Substance:

Ethylene is a colorless gas with a sweet odor and taste and is lighter than air.

Table 1: Chemical and Physical Properties of Ethylene

Property	Value[a]
Physical State and Appearance	Colorless gas with a sweet odor. Pressurized liquid when shipped below 50°F.
Odor	Sweet odor
Taste	Sweet taste
Color	Colorless
Molecular Weight	28.05 g/mol
Solubility	Slightly soluble in water, 131 mg/L at 25 °C. Very soluble in ethanol, ether; soluble in acetone, benzene.
Boiling Point	-103.7 °C
Melting Point	-169.0 °C
Vapor Pressure	0.978 (lighter than air)
Stability	Stable under recommended storage conditions.

[a] Source: (National Institutes of Health: https://pubchem.ncbi.nlm.nih.gov/compound/6325)

Specific Uses of the Substance:

Ethylene acts as a plant hormone and is typically associated with fruit ripening (see *Action of the Substance,* below). In some plants, ethylene can also induce plant tips (apical meristems) to develop flowers (Davies, 2010).

Crop producers apply ethylene gas in the field to induce flowering in pineapples, as allowed at §205.601(k) (NOP, 2000). Using specialized equipment mounted to a tractor with a boom, producers inject ethylene gas (2.25-3.5 kg/ha) into water (7014 L/ha) and activated charcoal. As the ethylene bubbles through the water, it is partially hydrolyzed and partially adsorbed by the charcoal. After the mixture is applied via flood nozzles, ethylene slowly releases from the carbon/water mix, where it is then absorbed by the plants. Two applications are usually made on consecutive nights (NOP, 2000).

Crop producers and handlers also use ethylene to accelerate the ripening of tropical fruit, and to "degreen" citrus fruit. This can be done at distribution points or in special ripening rooms on-site at farms, using either gas cylinders to provide metered amounts of the gas, or catalytic generators to produce the gas from ethanol. These activities are "post-harvest" uses, covered under the listing at §205.605(b). These uses are discussed further in the separate 2023 Handling technical report for Ethylene.

Ethylene products are labeled for ripening a variety of crops, including avocados, kiwis, melons, mangos, papayas, pears, persimmon, pineapple, stone fruits, tomatoes, and other fruiting vegetables (Livingston, 2005). Ethylene products are also labeled for sprout suppression in stored potatoes (Airgas, 2011), and to accelerate flue curing of tobacco (Livingston, 2008). An earlier Technical Advisory Panel Review mentioned use of ethylene to improve the quality of bean sprouts in commercial production (NOP, 1999a). However, no current EPA registrations were found for this use (NPIRS, 2022).

For non-organic use, ethylene is also permitted for soil injection to control witchweed (*Striga* spp.) in vegetable and field crops (40 CFR 180.1016).

Outside of agriculture, ethylene is used as a precursor chemical in the manufacture of several plastics, including polyethylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride (Zhao et al., 2018). Ethylene is also used as an anesthetic, and a refrigerant (Zimmerman & Waltz, 2011).

Approved Legal Uses of the Substance:

Environmental Protection Agency (EPA)

Ethylene is considered a plant growth regulator (pesticide) and has an exemption from the requirement of a tolerance for residues at 40 CFR 180.1016:

> §180.1016. Ethylene is exempted from the requirement of a tolerance for residues when:
>
> a. For all food commodities, it is used as a plant regulator on plants, seeds, or cuttings and on all food commodities after harvest and when applied in accordance with good agricultural practices.

In the United States, pesticide manufacturers must register their products with the EPA as well as the appropriate state pesticide control agencies (EPA, 2022; NPIC, 2022).

USDA Animal Plant Health and Inspection Service (APHIS)

USDA APHIS has an active program to control witchweed, a parasitic plant that can significantly damage corn, rice, sorghum, and sugarcane. In 2021, APHIS worked with cooperating farmers to treat 999 acres out of an estimated 1,600 acres infested. Methods used included tillage, herbicides, hand pulling, and the use of ethylene gas injection to cause premature seed sprouting (USDA APHIS, 2022; EPA, 1995).

United States Food and Drug Administration (FDA)

FDA includes "treating to manipulate ripening" under the definition of "manufacturing /processing" at 21 CFR 117.5 and 21 CFR 112.3. These food safety regulations consider that "treatment to manipulate ripening of raw agricultural commodities (such as by treating produce with ethylene gas), and packaging and labeling the treated raw agricultural commodities, without additional manufacturing/processing, is within the 'farm' definition." This means that use of on-farm ripening rooms would not cause a farm to be considered a manufacturing facility, subject to additional regulation under FDA food safety rules.

Action of the Substance:

Ethylene is a plant growth regulator that is produced naturally by plants and has effects on many aspects of plant growth, development, and survival, including (Chang, 2016):

- seed germination
- shoot growth
- root development
- flowering, sex determination
- fruit ripening
- abscission of leaves and fruits
- senescence of flowers and leaves

Ethylene also has a role in plant adaptation to a variety of stresses, such as drought, flooding, pathogen attack and high salinity (Chang, 2016).

Ethylene is biosynthesized by a series of reactions which transform methionine into ethylene:

L-methionine
↓
S-adenosylmethionine (SAM)
↓
1-aminocyclopropane-1-carboxylic acid (ACC)
↓
ethylene

The biosynthesis process is regulated at each step by enzymes and other factors that control the amount of ethylene produced (Chang, 2016; Schaller, 2002). Ethylene can promote or inhibit growth and senescence processes in plants, depending on its concentration, timing of internal production or external application, and the plant species (Iqbal, 2017). The specific mechanism of action of ethylene in plants continues to be under active investigation. Plants increase the production of ethylene-related enzymes in response to environmental cues and stresses such as wounding, drought, low temperature, or flooding (Chang, 2016).

In general, ethylene gas is produced in fruit when physiological maturity is reached. In pineapple, the gas is generated at vegetative maturity of the plant. Application of ethylene has the effect of triggering and synchronizing the flowering and fruiting cycle to occur sooner than it would naturally (Van de Poel et.al, 2009). In the case of fruit ripening, natural production of ethylene in plant tissue increases rapidly. The gas triggers the chemical changes (e.g., starch conversion to sugar, cell wall softening) which take place at ripening. Climacteric fruits are capable of ripening after harvest, and generally show a response to exogenous ethylene. This causes them to ripen more rapidly and evenly, and also to produce more ethylene naturally (Maduwanthi & Marapana, 2019).

Combinations of the Substance:

Farmers typically mix ethylene with water when spraying it on pineapple, often adding activated charcoal (NOP, 2000). Activated charcoal is thought to partially absorb the ethylene and slowly release it to plants after application. Van de Poel et. al (2009) evaluated different rates of application of activated carbon in water mixed with ethylene gas and found that only high rates (5% of the solution) were effective at increasing ethylene absorption. Commercial doses applied at rates of 0.286% (20 kg activated carbon /7000 L water/ha) had no effect on flower induction. However, Soler et al. (2006) successfully used a rate of 5% activated carbon in small hand-held units designed to deliver ethylene mixed with water and handled by a single operator.

There are currently five active registrants of agricultural grades of ethylene gas in the U.S., with seven labeled products. They are labeled with ethylene concentrations ranging from 98.5% to 99.9%, with the remainder being impurities (NPIRS, 2022; IARC, 1994). One product (Banana Gas 32, Praxair) is labeled as containing 6.3% ethylene and 93.7% carbon dioxide.

Status

Historic Use:

The NOP added ethylene to the National List as published December 2000 for use to regulate flowering in pineapple (FR 65 80547). It was also included for post-harvest handling to ripen tropical fruit. In November of 2003, the NOP made a change to the annotation for the post-harvest allowance to also allow for degreening of citrus (68 FR 61987). Prior to the USDA regulations, private certifiers and state programs in the U.S. generally allowed ethylene for use to ripen bananas, and some permitted ripening of mangos (NOP, 1999b). A petition to modify the handling annotation to permit use for ripening pears was received by NOP in 2008, but the National Organic Standards Board (NOSB) voted to reject this use in November 2008.

Early uses of natural ethylene included the gashing (wounding) of figs in the Middle East to promote fruit growth and ripening, and the use of weights to encourage bean sprout thickening. Both cases resulted in stress-induced ethylene production by the plants (Abeles, 1992). Farmers have long used smoke or off-gassing from ripe fruit to hasten fruit ripening before ethylene was recognized as the active agent. Pineapple growers accidently discovered in 1874 that smoke in greenhouses in the Azores caused pineapple flowers to develop (Collins, 1960; Rainha, 2013). In the 1920s, growers in Puerto Rico used smudge fires beneath muslin cloth covering pineapple. By 1932, researchers found that the active ingredient in smoke was ethylene (Bartholomew et al., 2003). According to Bartholomew (2014), over the next decades the Hawaiian pineapple industry investigated many different compounds and growth regulators to induce flowering but found that the effectiveness was related to the fact that these compounds were precursors or stimulators of ethylene. Researchers also found that aminoethoxyvinlyglycine (AVG), an ethylene inhibitor, prevented flower induction.

The pineapple plant is a unique crop in that flowering can be induced by external application of the plant growth regulator, ethylene. Pineapple is grown in tropical and subtropical countries, and the time from planting to harvest can range from 12 months in tropical regions to almost 30 months in the cooler subtropics. “Forcing” of pineapple flowering (causing pineapple plants to flower all at once in a predictable time period) using ethylene has become an important agronomic practice to ensure uniform flowering and thus time of ripening and reduce production costs. It is especially important for synchronizing varieties grown for the fresh market (Chang, 2011; Van de Poel et al., 2009), and it is now common to force pineapple crops in all months of the year. In the subtropical regions, the natural induction of flowering can be caused by cooler winter temperatures, which can interfere with timing of forcing and lead to yield losses, potentially producing a glut of fruit in the summer and lack of fruit in the fall (Bartholomew, 2014). Hawaii was slow to adopt the use of ethylene in the 1950s because the industry there relied on natural flower induction to provide a broad harvest period in the summer that was compatible with harvest labor availability from students on summer break. Hawaii was primarily growing the ‘Smooth Cayenne’ variety for canning at that time, which had better quality when harvested in the summer (Bartholomew, 2014).

The use of artificial flower induction led to the development of the fresh fruit export market, with the ability for year-round production (Bartholomew, 2014; Chang, 2011). The popular MD-2 “Gold” variety produces high quality fruit year-round but is sensitive to natural flower induction (can flower naturally and interfere with timing of ethylene induced flowering). This is especially a problem when grown in cooler subtropical regions, and the control of natural induction has become a highly researched issue. Natural flower induction interferes with the forcing process by spreading out the harvest period, and results in fruit that are too small or too few in number to be worth harvesting (Li, 2022; Bartholomew, 2014; Bartholomew, 2018; Reinhardt, 2019).

Organic Foods Production Act, USDA National Organic Program regulation:

Organic Foods Production Act of 1990

Ethylene is not specifically mentioned in the Organic Foods Production Act. It is not specifically mentioned as an allowed class of materials at 7 U.S.C. 6517(c)(1)(B). However, it could be considered a “production aid,” which is a permitted class.

USDA Organic Regulations

Ethylene is approved for organic crop use:

> 7 CFR 205.601(k) as plant growth regulators. (1) Ethylene gas - for regulation of pineapple flowering.

Ethylene is also approved for organic handling use:

> 7 CFR 205.605(b) Ethylene - allowed for postharvest ripening of tropical fruit and degreening of citrus.

International

Canada, Canadian General Standards Board – CAN/CGSB-32.311-2020 Organic Production Systems Permitted Substances Lists
Ethylene is allowed for organic use under the Canadian Organic Production Systems, General Principles and Management Standards (CAN/CGSB-32.310-2020). Clause 1.5 states that plant growth regulators are prohibited except if listed in the Permitted Substances Lists (PSL), CAN/CGSB-32.311.

The PSL states at Table 8.3 - Post-harvest substances:

> "Ethylene: For post-harvest ripening of tropical fruit and degreening of citrus and to control sprouting of potatoes post-harvest in holding bins."

CODEX Alimentarius Commission – Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)
Codex guidelines do not mention the use of ethylene, and it is not included in Annex 2 as a permitted substance (Codex, 2007).

European Economic Community (EEC) Council Regulation – EC No. 834/2007, 889/2008, 2018/848 and 2021/1165
Ethylene is permitted as listed in Annex 2, Pesticides — plant protection products.

> "Ethylene: Degreening bananas, kiwis and kakis; Degreening of citrus fruit only as part of a strategy for the prevention of fruit fly damage in citrus; Flower induction of pineapple; sprouting inhibition in potatoes and onions" (EEC, 2008).

The most current EU organic standards, 2018/848, which became enforceable in January 2022, permit ethylene under 2021/1165 Annex I, "Active substances contained in plant protection products authorised for use in organic production as referred to in point (a) of Article 24(1) of Regulation (EU) 2018/848:"

> "Only on bananas and potatoes; however, it may also be used on citrus as part of a strategy for the prevention of fruit fly damage."

Japan Agricultural Standard (JAS) for Organic Production
The JAS standards (JAS, 2017) list ethylene in Appended Table 5, as:

> "Ethylene, Limited to those used for ripening bananas, kiwifruits and avocados after harvest."

IFOAM – Organics International
Ethylene is listed as approved in Appendix 4 – Table 1: List of approved additives and processing/post-harvest handling aids.

> "Ethylene: De-greening of citrus and ripening." (IFOAM, 2018)

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?
Ethylene is used in crop production as a plant growth regulator, which is not an explicitly listed category in OFPA. It could be considered a crop production aid. Ethylene does not appear on 2004 EPA List 4 but does appear at 40 CFR 180.1016 as a material exempt from the requirement of a tolerance for residues. EPA allows it for use without limits on all food commodities as a plant growth regulator on plants, seeds,

or cuttings. It is also permitted without limits on all food commodities after harvest, when applied in accordance with good agricultural practices. It also is specifically allowed for soil injection on certain crops to cause premature germination of witchweed seeds (EPA, 1999).

Evaluation Question #2: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. 6502(21)).

Thermal cracking

Ethylene is the petrochemical produced in the largest quantities worldwide (IARC, 1994). In 2014, world ethylene production was 134 million (metric) tons (Lazonby, 2017). As of 1994, over 95% of worldwide annual production is based on thermal "cracking" of petroleum hydrocarbons with steam (IARC, 1994). These fractions are obtained from drilling (or hydrofracturing) of oil or natural gas. Thermal cracking (sometimes referred to as pyrolysis) is a chemical process by which long chain hydrocarbons with higher molecular masses are converted to short chain hydrocarbons of lower molecular mass.

Various feedstocks, including ethane, propane, butane, naphtha, and gas oil are used to produce ethylene, depending on availability, price, and products desired (Lazonby, 2017). Naphtha is the principal raw material used in western Europe and Japan, accounting for over 80% of the ethylene produced. Ethane is the primary feedstock in the U.S., followed by propane, naphtha, gas oil, and butane (Zimmerman & Waltz, 2011).

In thermal cracking the feedstock gases (ethane, propane or butane) or the liquids (naphtha or gas oil) are preheated and vaporized and are mixed with steam and heated to 1050-1150 K (777-877 °C) in a tubular reactor. The high temperature and pressure cause the long chain hydrocarbon to be converted to low relative molecular mass alkenes plus by-products (Lazonby, 2014).

World use of ethylene (134 million tons, 2014) (Lazonby, 2017)

- 60% - polyethylene
- 16% - ethylene oxide
- 11% dichloro-1,2-ethane (precursor to PVC, polyvinyl chloride)
- 5% - ethylbenzene (precursor to polystyrene)

A "relatively small" amount of industrially produced ethylene gas is used for agriculture and controlled ripening (IARC, 1994). No estimate was found of the actual amount used in agriculture or post-harvest ripening per year.

Catalytic cracking

Catalytic cracking uses a catalyst, typically a zeolite, which adsorbs the long-chain hydrocarbon feedstocks and removes hydrogen atoms. [1] This causes the long chains to split into shorter chain molecules with double bonds, which are useful to the petrochemical industry. The feedstock is gas oil, which is vaporized, passed through a fine zeolite powder, and heated to 700-800 K (427 - 527 °C) in a reactor. The products behave like a fluid and continuously flow out of the furnace with the cracking products. The temperature, residence time, and the catalyst determine the product proportions (Lazonby, 2014).

Dehydration of ethanol

Dehydration of ethanol is another commercial route to ethylene (IARC, 1994; Zimmerman & Waltz, 2011; Fan 2013). In the catalytic dehydration of ethanol to form ethylene, an acid catalyst first protonates the hydroxyl group, which leaves as a water molecule. The conjugate base of the catalyst then deprotonates the methyl group, and the hydrocarbon rearranges into ethylene (Fan, 2013). This method is not used

[1] Zeolites are hydrated aluminum silicate compounds that may occur naturally as minerals but may also be produced synthetically.

commonly to produce large volumes of ethylene as it is endothermic with a high optimal reaction temperature (180-500 °C), which makes the ethylene expensive to produce. Dehydration of bioethanol is occurring in Brazil and India and holds promise for producing ethylene from non-fossil fuel sources (bioethanol from sugar cane or cellulose). At present the output is relatively limited, and used for further production of polyethylene (Fan, 2013; Lazonby, 2017; Schill, 2010).

Catalytic generators

Small catalytic generators are used in sealed ripening rooms to dehydrate ethanol into ethylene and can deliver controlled levels of ethylene gas to ripen fruit, e.g., 100-150 ppm for bananas. (NWHort 2008, Catalytic Generators 2022). This process uses dehydration of ethanol by passing it over a bed of solid catalyst held at high temperatures. The catalysts are typically activated alumina and phosphoric acid or zinc oxide with alumina (Kays & Beaudry, 1987).

Evaluation Question #3: Discuss whether the petitioned substance is formulated or manufactured by a chemical process or created by naturally occurring biological processes (7 U.S.C. 6502(21)).

As described in *Evaluation Question* #2, the principal source of commercial ethylene is from thermal or catalytic cracking of hydrocarbon feedstocks such as natural gas or crude oil. During this process, chemical bonds within the hydrocarbon molecules are broken, and a different chemical substance is produced.

Catalytic cracking uses a catalyst, typically a zeolite, which absorbs the long-chain hydrocarbon feedstocks by removing hydrogen atoms and causes the long chains to split into shorter chain molecules with double bonds (Lazonby, 2014). Small catalytic generators dehydrate ethanol by a similar process (Kays & Beaudry, 1987).

All of these methods involve reactions that produce a chemically changed substance (ethylene) from either petroleum feedstocks, or from dehydration of ethanol mediated by catalysts. Thus, all these forms should be considered synthetic (NOP, 2016a) and from nonagricultural sources (NOP, 2016b).

Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment (7 U.S.C. 6518(m)(2)).

Ethylene is ubiquitous in the environment, arising from both natural and man-made sources. Major sources are natural emissions from vegetation; as a product of burning vegetation, agricultural wastes and refuse, and the incomplete combustion of fossil fuels; and from releases during the production and use of ethylene (IARC, 1994).

Total annual emission of ethylene from the global surface was estimated in 1994 to be 18-45 million (metric) tons per year (19.9 - 49.6 million U.S. tons), of which approximately 74% is released from natural sources and 26% from anthropogenic sources (see **Figure 2**, below; IARC, 1994). Burning of biomass to clear land for agriculture or other uses is believed to be the largest anthropogenic source of ethylene emissions (77%); the combustion of various fossil fuels also accounts for a significant fraction (21%) of anthropogenic emissions (IARC, 1994). No newer data on global emissions were identified in the literature review for this report.

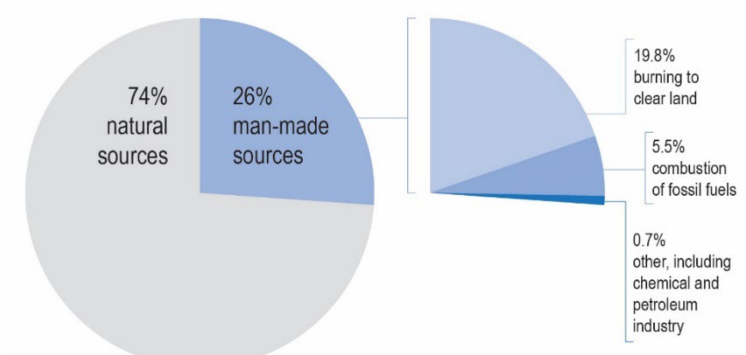

Figure 2: Estimated tons of global surface emissions of ethylene in 1995 (IARC, 1994).

According to the U.S. EPA Toxic Release Inventory, in 2021 the total release of ethylene in air emissions in the United States was 18.2 million pounds (9,100 tons) (EPA, 2021). Of that, 17.2 million pounds was emitted by the chemical manufacturing industry, and less than 1 million was from the petroleum industry. For comparison, this is only a small fraction of the amount of ethylene released globally in 1994 (18-45 million *tons*). The International Agency for Research on Cancer of the World Health Organization (IARC) monograph cites 1993 data from EPA showing that airborne emissions at that time in the U.S. were at the level of 38.4 million pounds. Health Canada (2016) also noted that emissions from manufacturing have decreased by half from 2000-2009, due to recycling and improved technology. Emissions from combustion engines have also dropped substantially in that time frame.

The half-life of ethylene is 1-28 days in water, 1.01 days in air, and 1-28 days in soil (HealthCan, 2016). Ethylene is readily oxidized in the atmosphere with a theoretical global residence time in the troposphere ranging from two to four days. There are also numerous chemical reactions associated with the breakdown of ethylene that may decrease its half-life to just a few hours (HealthCan, 2016).

When released to air, ethylene exists solely as a gas in the atmosphere (HealthCan, 2016). Gas-phase ethylene degrades in the atmosphere by reaction with photochemically-produced hydroxyl radicals. The half-life for this reaction in air is around two days. Ethylene will also be degraded in the atmosphere by reaction with ozone and nitrate radicals; the half-lives of these reactions are 6.5 and 190 days respectively. Ethylene is not susceptible to direct photolysis by sunlight (NCBI, 2022b HSDB).

Ethylene reacts in air primarily with hydroxyl radicals (OH•) but it can also react with nitrate ions (NO_3^-) and ozone (O_3). The oxidation of ethylene can generate nitrogen dioxide (NO_2) which can later form ozone (HealthCan, 2016).

Ethylene reacts with ozone in the atmosphere to form water, carbon dioxide, carbon monoxide and - formaldehyde. This reaction reduces ozone levels in the atmosphere (Abeles, 1992). Reaction of ethylene with oxygen produces carbon monoxide, ethane, propylene, acetaldehyde, propanal, butanal, hydrogen, and ethylene oxide (Abeles, 1992).

When released to soil, ethylene is likely to be highly mobile, based upon its estimated soil adsorption coefficient (Koc of 13) (NCBI, 2022b). [2] Volatilization from moist or dry soil surfaces is also an important fate. If released into water, ethylene is unlikely to adsorb to suspended solids and sediment, based upon the estimated Koc. Using model data, researchers estimated that the half-life of ethylene due to volatilization is two hours in rivers and two days in lakes. Hydrolysis is not an important environmental fate process since this compound lacks functional groups that hydrolyze under environmental conditions (pH 5 to 9) (NCBI, 2022b).

Health Canada reviewed several models for bioaccumulation and bioconcentration and concluded that ethylene is neither persistent nor bioaccumulative in the environment (HealthCan, 2016). An estimated bioconcentration factor of 2.6 suggests the potential for ethylene to bioconcentrate in aquatic organisms is low (NCBI, 2022b). The U.S. EPA last reviewed ethylene in 1992 and stated that since it is naturally occurring and "has a nontoxic mode of action" that it has been classified as a biochemical. EPA waived ecological effects studies for both indoor use and outdoor use on crops, citing the classification as a biochemical, use patterns, and low application rates on pineapple (EPA, 1992).

Evaluation Question #5: Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants.

Human health effects are discussed under *Evaluation Question #10.*

[2] Koc measures the mobility of a substance in the soil, adjusted for carbon content. A high number (over 4.5) means the substance is strongly adsorbed onto the soil and organic matter (ChemSafety, 2022).

The Health Canada review (2016) found that ethylene has no effects on invertebrates or birds, which are the animals most likely to be exposed to the substance. Health Canada did not expect that ethylene would be released to water but did not find adequate empirical toxicity studies on aquatic species. Health Canada's review of mammalian studies also found that the concentrations of ethylene tested to determine adverse levels in rats are considerably higher than concentrations expected in the Canadian environment (HealthCan, 2016).

Ethylene has been known to damage plants when they are exposed to gas leaks or combustion engine exhaust (Abeles, 1992). Health Canada noted that terrestrial plants are highly sensitive to ethylene in air and considered that was the primary risk for environmental concerns. They performed a risk quotient analysis based on industrial monitoring for four years and found on average one occurrence per year that had potential to be harmful to plants. The agency concluded that there is little risk of harm to the environment or to organisms since the substance is not present in quantities or concentrations that could cause long term harmful effects on the environment or biodiversity (HealthCan, 2016).

Evaluation Question #6: Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. 6518(m)(3)).

The cracking of naphtha or of ethane to manufacture ethylene is highly energy-intensive (Ghanta et al., 2014; Zimmerman & Waltz, 2011). The energy expended during the extraction and ocean-based transportation of fossil fuel sources (crude oil and natural gas) contributes significantly to adverse environmental impacts such as greenhouse gas emissions, acidification of precipitation, and eco-toxicity (air and water). A life-cycle assessment comparing environmental impacts for thermal and steam cracking of hydrocarbons to dehydration of bioethanol from corn or biomass found similar requirements for energy and overall impact on the environment. The fuel burning to produce energy at power plants was deemed by far the biggest contributor to the various adverse environmental impacts for all methods (Ghanta et al., 2014).

Zimmerman & Waltz (2011) note that the manufacture of ethylene does produce "significant" amounts of carbon dioxide and note that this may be a factor in the development of alternative technologies for production of ethylene. Zhao et al. (2018) looked at the production life cycle for ethylene and state that the chemical industry, which is highly energy-dependent, is responsible for 16% of direct global CO_2 emissions. Ethylene, as one of the most important chemicals in use, consumes 30% of the total energy of the chemical industry. This study found that while China reduced CO_2 emissions by 29.4% per ton of ethylene produced from 2000-2016 due to improvements in technology, carbon dioxide emissions due to ethylene production continue to increase overall due to increased demand (Zhao et al., 2018).

Petroleum refineries are a major source of hazardous and toxic air pollutants such as benzene, toluene, ethylbenzene, and xylene (EPA, 2003). They are also a major source of other air pollutants: particulate matter, nitrogen oxides, carbon monoxide, hydrogen sulfide, and sulfur dioxide. Refineries also release natural gas (methane) and other light volatile fuels and oils. Some of the chemicals released are known or suspected cancer-causing agents, responsible for developmental and reproductive problems. Refineries are also potential major contributors to ground water and surface water contamination. Some refineries use deep-injection wells to dispose of wastewater generated inside the plants, and some of these wastes end up in aquifers and groundwater (EPA, 2003).

When synthetic ethylene gas is used on agricultural crops, any excess will volatilize in the air. Since ethylene is a gas at environmental temperatures, this is the primary route of exposure to the environment. Health Canada considered environmental modelling studies and found that ethylene released to the air will remain in the air, and that only negligible amounts will partition to soil, water and sediment (HealthCan, 2016).

Evaluation Question #7: Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions (7 U.S.C. 6518(m)(1)).

Ethylene used in crop production is in gas form and is a synthetic analog of the natural ethylene produced by plants. The U.S. EPA considers that outdoor use for soil injection (witchweed control) and pineapple sprays will result in negligible exposure to aquatic and terrestrial organisms (EPA RED, 1992).

Ethylene should not be mixed with ozone, peroxides, other oxidizing agents, or with strong acids, which could cause explosive reactions (NJDOH, 2003; NOAA, n.d.).

Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock (7 U.S.C. 6518(m)(5)).

Ethylene applied to crops will volatilize if not absorbed by the plant, and so the contribution to soil levels will be minimal. Ethylene in the atmosphere has an estimated half-life of two days (NCBI, 2022b). Natural soil ethylene levels are often higher than those in the air, and often associated with waterlogged soils (Abeles, 1992). Ethylene is readily metabolized by soil organisms, particularly by *Mycobacterium paraffinicum,* which is reportedly efficient enough to remove ethylene from soils (Abeles, 1992).

Health Canada (2016) reviewed studies on ethylene impact on crop plants and found that air concentrations between 5.6 and 12 $\mu g/m^3$ had both positive and negative effects on various plant species. Some cereals, such as barley and oats, appear to be highly sensitive to ethylene at air concentrations as low as 34.4 $\mu g/m^3$, showing a 63% reduced seed production. Tomatoes show slight curling of leaves at 11.45 $\mu g/m^3$, and peas show a reduction in the elongation of the epicotyl during germination at this concentration, while canola has increased seed production at 12$\mu g/m^3$ (HealthCan, 2016).

Evaluation Question #9: Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment (7 U.S.C. 6517(c)(1)(A)(i) and 7 U.S.C. 6517(c)(2)(A)(i)).

Ethylene is a natural substance emitted by plants. When synthetic ethylene gas is applied in water to plants, it will be absorbed by the plant or volatilize as a gas. As a plant growth regulator, it is used in very small amounts: generally, 800 g per hectare (0.71 lbs. per acre) applied in 6-8000 liters of water (Bartholomew, 2003). The Food and Agriculture Organization of the United Nations estimates that in 2021, there were 1,046,712 hectares of pineapples grown worldwide (FAO, 2022). If every hectare in the world was treated with 800 grams of ethylene (unlikely, as the harvest takes 12-18 months from flower induction), that would result in application of 837,369 kg (1,846,082 pounds) totally.

For comparison, according to the U.S. EPA Toxic Release Inventory, the total release of ethylene as airborne emissions in the U.S. was 18.2 million pounds in 2021. Of that, 17.2 million pounds were emitted by the chemical manufacturing industry, and 0.7 million pounds were from the petroleum industry.

Effects on mammals, invertebrates, birds, and plants are discussed under *Evaluation Question #5*.

Evaluation Question #10: Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. 6517(c)(1)(A)(i), 7 U.S.C. 6517(c)(2)(A)(i)) and 7 U.S.C. 6518(m)(4)).

The main safety concern in relation to ethylene use has been due to the explosive nature of the gas in the air. This is of primary concern in design and operation of ethylene treatment facilities. The EPA, local fire marshal rules, and insurance companies all have very specific labelling and registration requirements for the ethylene itself and the process used to apply it, down to the electrical wiring and piping used in ripening rooms (Sherman, 1985). The gas is explosive in air at concentrations from 3.1% to 32% (31,000 to 320,000 ppm). The minimum explosive concentration (3.1%) exceeds the suggested ethylene concentrations for tomato ripening and citrus degreening respectively by 200 and 6,200 times (Sherman, 1985). The "banana gas" (cylinders with 6% ethylene content) and catalytic generator sources of ethylene are considered the safest because they are more easily monitored, but explosive accidents have happened in the past, and operators should be well trained and prepared (Sherman, 1985).

Ethylene is highly flammable and explosive. Overexposure causes headache, drowsiness, and muscular weakness (NOAA, n.d.). High concentrations of ethylene (>1000 ppm) can cause dizziness or light-headedness. For several decades in the 1900s, ethylene was used as a general anesthetic (Chang, 2016; EPA, 1992).

Ethylene is classified as a simple asphyxiant and acts primarily to limit oxygen (OSHA, 2018). The U.S. Department of Labor Occupational Safety and Health Administration (OSHA) limits exposure levels in OSHA Construction and Maritime standards. The limiting factor is the available oxygen which shall be at least 19.5% in construction and at least 18% for maritime standards (OSHA, 2018).

Exposure to 37.5% ethylene for 15 min may result in marked memory disturbances (NCBI, 2022b). Humans exposed to as much as 50% ethylene in air, where the oxygen availability is decreased to 10%, experienced a loss of consciousness. In fatal human intoxication, ethylene affects the respiratory center of the brain and kills by suffocation. In workers chronically exposed, ethylene has been associated with a decrease in maximum arterial pressure, slower pulse, decreased visual-motor response, hearing and smelling loss, and problems with bodily temperature control (NCBI, 2022b).

Occupational exposure to ethylene may occur through inhalation and dermal contact at workplaces where ethylene is produced or used. Monitoring data indicate that the general population may be exposed to ethylene via inhalation of ambient air and smoking cigarettes (NCBI, 2022a; NCBI, 2022).

According to the National Institutes of Health Hazardous Substance Database, there is inadequate evidence in humans for the carcinogenicity of ethylene, and it is "not classifiable as a human carcinogen" (NCBI, 2022b).

Based on *in vivo* and *in vitro* studies, ethylene does not induce gene mutations (HealthCan, 2016). Using rats as a model organism, these studies show that ethylene is not carcinogenic when inhaled over a two-year period. In addition, epidemiology studies do not show evidence of cancer in exposed workers, although these studies are limited. For other non-cancer health effects, the "lowest-observed-adverse-effect concentration" (LOAEC) for inhalation exposure in rats is 11,500 mg/m^3 (10,000 ppm) based on slight nasal effects observed in rats in a 13-week inhalation study (HealthCan, 2016).

Health Canada compared the upper bounds of estimates of exposure from ethylene in indoor and outdoor locations[3] to the critical effects levels observed in the literature and concluded that ethylene does not enter the environment in enough quantity or concentration to be of concern for human health (HealthCan, 2016).

Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. 6517(c)(1)(A)(ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. 6518(m)(6)).

Pineapple growers discovered by accident in the Azores in 1874 that greenhouse plants could be forced into flower with smoke, and growers adopted the practice as a way to schedule fruiting when prices were high (Bartholomew, 2014). In the Azores as of 2013, pineapple was still grown in greenhouses and forced with smoke from burning of dried vegetation and wood chips. The carbon materials are placed in metal cans and burned for several hours in the evening, then vented the next day for a period of 9-21 days. This appears to be a very limited-volume, high-value specialty product, exported mainly to Portugal for the winter holidays. Reportedly, 40% of the crop is certified organic. Production has declined from a peak in the 1930s due to development pressure and competition from lower-cost production methods in Costa Rica, Brazil, Africa, and the Philippines (Rainha et al., 2013). The production practices are regulated by the EU Technical Committee on Certification and Control for Azorean pineapple as a Protected Designation of Origin product (Bartholomew, 2014).

[3] Testing was done in both urban and rural locations, though not specifically in crop or post-harvest treatment locations.

Once it was discovered that ethylene was responsible for the flower induction effects of smoke in the 1930s, the burning of wood or other carbon sources was not used for outdoors commercial pineapple production (Bartholomew, 2014). It is likely impractical for use on larger scale outdoor operations and would contribute to air pollution via release of particulates and carbon dioxide to the atmosphere.

Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. 6518(m)(6)).

The 2011 limited scope technical report discussed research done in Taiwan (Maruthasalam et al., 2010) to test use of chilled water or ice as a treatment for flower induction. Subsequent research has shown inconsistent results using these techniques (Chang et al., 2011). The researchers hypothesized that the chilling technique only works when night temperatures are cooler than 20 °C for 2-3 days before treatment, as well as for the duration of the treatments (ice cold water applied three or four times at 24-hour intervals). Soler et al. (2018) noted a report of trials in Costa Rica of chilled ice water or ice that did not give consistent results.

Pineapples can be grown without the use of artificial flower induction. However, relying on natural flower induction would drastically reduce the ability of tropical and subtropical producers to export marketable quantities of fresh organic fruit to other parts of the world. As noted in the limited scope technical report for ethylene, (NOP, 2011) the market for organic pineapple in the EU and the U.S. has increased steadily in the last decades, and some have attributed the growth in large part to the approval of ethylene for flowering in 2002 in the U.S. and 2005 in the EU (NOP, 2011; Pay, 2009).

A search to confirm if plant breeders have developed varieties that produce pineapples more consistently with natural flowering was conducted as part of this report. However, we found no literature on breeding pineapple for consistent natural flowering. Instead, there is a large effort to breed for *insensitivity* to natural flower induction, so that the plants will respond uniformly to ethylene applications (Li, 2022; Young, 2016).

Researchers in Benin looked at various methods to improve pineapple quality in order to increase the export market to Europe (Fassinou Hotegni, 2015). They compared systems that did not use artificial flower induction with those that did. Although they found that natural flower induction resulted in higher fruit weight and a greater percent that met the quality grade for export, it came at a "huge cost." This was due to a very long time from planting to flowering and harvest, the need for multiple harvests, and a low proportion of plants producing fruit. The study concluded that it would be better for growers to focus on cultural methods such as improved planting stock and use of organic manures and other fertilizers during the vegetative stage and manage the timing of flowering and fruiting with application of ethylene or related compounds (Fassinou Hotegni, 2015).

No other literature was found that explored alternative cultural practices to the use of ethylene in pineapple production.

Report Authorship

The following individuals were involved in research, data collection, writing, editing, and/or final approval of this report:

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All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.

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