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White Paper

Methanol Use in Wastewater Denitrification

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July 2012

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Chemical Abbreviations

C	carbon
CH_3OH	methanol
CH_3CH_2OH	ethanol
CH_3COOH	acetic acid
CO_2	carbon dioxide
DO	dissolved oxygen
H^+	hydrogen ion
HCO_3^-	bicarbonate ion
HNO_3	nitric acid
H_2	nitrogen gas
H_2CO_3	carbonic acid
H_2O	water
N	nitrogen
N_2	nitrogen gas
Nr	reactive nitrogen
NH_3	ammonia
NH_4^+	ammonium ion
NO	nitric oxide
NOx	nitrogen oxides
N_2O	nitrous oxide
NO_2^-	nitrite ion
NO_3^-	nitrate ion
O_2	oxygen
O_3	ozone
OH^-	hydroxide ion
PAN	peroxy acetyl nitrates
TN	total nitrogen
TP	total phosphorous

Acronyms and Abbreviations

AOB	ammonium oxidizing bacteria
BMP	best management practice
BNF	biological nitrogen fixation
BOD	biochemical oxygen demand
CL	critical load
CWA	Clean Water Act
DO	dissolved oxygen
EPA	U.S. Environmental Protection Agency
EPA	U.S. Environmental Protection Agency
EU	European Union
EUWFD	European Union Water Framework Directive
GHG	greenhouse gases
ha	hectare
HRT	hydraulic residence time
IRIS	Integrated Risk Information System
kg	kilogram (10^3 grams)
LCA	life-cycle assessment
MGD	million gallons per day
mg/L	milligrams per Liter
MLE	Modified-Luck Ettinger (process)
NFPA	U.S. National Fire Protection Association
Nr	reactive nitrogen
NTP	National Toxicology Program
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
$PM_{2.5}$	particles less than 2.5 micrometers in diameter
POTW	publicly owned treatment works
ppb	parts per billion
ppm	parts per million
RAS	return activated sludge
SBR	sequencing batch reactor
SHM	*Methanol Safe Handling Manual*
SRT	solids residence time
Tg	teragram (10^{12} grams)
TMDL	total maximum daily load
TRACI	Tool for the Reduction and Assessment of Chemical and other environmental Impacts
TSS	total suspended solids
TWA	time-weighted average
WWTP	wastewater treatment plant

Executive Summary

The discharge of reactive nitrogen, Nr, into surface water has contributed to eutrophication (excessive plant/algae growth) and coastal hypoxia (oxygen depletion) in more than 400 estuaries worldwide, with few signs of improvement. Although much of the Nr that reaches these systems originates as agricultural and urban runoff and atmospheric deposition, an important point source of Nr to these ecosystems is effluent from wastewater treatment plants (WWTPs).

In order to meet mandated ammonia discharge requirements, most municipal systems in the United States practice nitrification (oxidation of ammonia to nitrites and nitrates), but only about 5 percent of Nr is removed through engineered denitrification treatment systems. A nitrogen removal system presents a method for removing a large portion of the nitrogen concentration from wastewater effluent before it is discharged. In an anoxic nitrogen removal system, an external carbon source, such as methanol, is often required to ensure that denitrification is maximized. This White Paper provides an overview of the use of methanol in the removal of nitrogen from wastewater.

Nitrogen in the Environment

Anthropogenic sources of reactive nitrogen (all forms of nitrogen except N_2) are currently three times as great as the nitrogen inputs from natural sources. There are three major sources: combustion processes, application of artificial fertilizers to farm and turf lands, and the purposeful planting of legumes.

Because of its complex chemistry, reactive nitrogen can be chemically transformed as it translocates to different parts of the environment, creating a cascading set of environmental impacts. Closure of the nitrogen cycle can be achieved only through denitrification—the conversion of nitrate and nitrite to $N_{2.}$ Although this occurs naturally, an important part of removing nitrogen from aquatic systems is engineered denitrification of wastewater.

Regulatory Climate for Nitrogen in Wastewater

The last several decades have seen a world-wide increase in the regulatory control of nitrogen. In the United States, the Clean Water Act incorporates both technology-based and water-quality-based levels of treatment. Historically, most WWTPs have treated to standards based on the ability of secondary treatment to meet effluent standards, such as 30 mg/L for both biochemical oxygen demand (BOD) and total suspended solids. As the impact of the macronutrients nitrogen and phosphorus on eutrophication became more apparent, the U.S. EPA began to put more emphasis on meeting water-quality-based standards. Given the regional nature of sources for impacted estuaries, the most effective way to control the amount of nitrogen effluents is through collaborative efforts of multiple jurisdictions. The Chesapeake Bay and Long Island Sound programs are examples of coordination by state and local agencies to reduce the total load of reactive nitrogen to regional water bodies, including the upgrading of WWTPs to include tertiary treatment to remove nitrogen from their effluents.

In Europe, the European Water Framework Directive (EU WFD) marked a shift in focus, from point-source control to an integrated prevention and control approach at the water-body level. Tertiary wastewater treatment has increased since 1990, although the percentage of wastewater treatment plants with tertiary treatment varies by region. This increasing trend in the use of tertiary wastewater treatment, coupled with the more stringent treatment objectives, suggests that this will be an expanding market. The EU WFD caused the discharge standard for nitrogen in water to decrease from 10 mg/L to 2.2 mg/L. The goal of this action is to “promote sustainable water use, protect the aquatic environment, improve the status of aquatic ecosystems, mitigate the effects of floods and droughts, and reduce pollution.” The two-step strategy to achieve the directive’s goals includes the adoption of new wastewater treatment technologies, including biological denitrification.

In the past 10–15 years, China has experienced rapid industrialization. With industrialization comes the need for discharge standards and more effective wastewater treatment. As of 2002, 35.5% of rivers in China were not suitable for drinking-water use due to pollution issues, which has led to a water shortage. Environmental legislation put in place in 2003 sets Class 1A effluent discharge standards at <5 mg/L ammonia nitrogen and <15 mg/L total nitrogen. As of 2002, only 39% of wastewater in China was being treated; the number grew officially to 59% as of 2008. Coupled with the new legislation, these statistics suggest that China represents an emerging market for tertiary wastewater treatment for nitrogen removal. In the last several years, almost a dozen existing WWTPs have been upgraded to biologically remove nitrogen using denitrification filters, with methanol as the supplemental carbon source.

Biochemistry of Biological Nitrogen Removal

Urea, fecal matter, and food processing wastes are the primary sources of nitrogen for municipal wastewater. Domestic wastewater typically has a total nitrogen content that is about one-fifth of the BOD, with typical nitrogen concentrations ranging from 20 to 70 mg/L. About 60% to 70% is ammonia-nitrogen, and 30% to 40% percent is organic nitrogen, with less than 1% nitrite and nitrate nitrogen (Tchobanoglous et al. 2003).

The removal of nitrogen in biological treatment systems consists of four basic steps. The first step is the conversion of organic nitrogen to ammonia in a process called ammonification. Ammonia is then converted to nitrate in a two-step aerobic process called nitrification—the conversion of ammonia to nitrite followed by the conversion of nitrite to nitrate. Finally, nitrate is converted to nitrogen gas by the anoxic process of denitrification.

Nitrogen Biological Removal Systems

In the past, wastewater treatment was focused on removing solids, measured as total suspended solids (TSS), and organics, measured as biochemical oxygen demand. The main objective was to prevent the depletion of oxygen because of the degradation of organics in water bodies receiving the treated wastewater. Over time, it became apparent that macronutrients—nitrogen and phosphorus—were the major cause of eutrophication in surface waters. Focus shifted to including nutrient removal at wastewater treatment plants, especially where eutrophication was a major concern.

The Clean Watersheds Needs Survey (CWNS) 2008 Report to Congress (U.S. EPA 2008) indicates that, of 17,749 treatment facilities, 848 (5%) currently treat their effluent for nitrogen removal, and an additional 595 (3%) are projected to need nitrogen removal treatment.

Biological removal of nitrogen can be carried out using various treatment configurations. It can be done using a single-unit process with various treatment zones or in separate stages. Suspended growth, fixed growth, or combined systems can be used. Whatever the treatment system used, they all require an aerobic zone for converting ammonia to nitrate and an anoxic zone for converting the nitrate to nitrogen gas. One of the more common approaches to retrofitting existing facilities is to extend the aeration period to allow for nitrification, followed by a filtration system for denitrification. Because organic carbon is consumed by denitrifying bacteria, mostly in the extended aeration process, it is often necessary to add a carbon source, such as methanol, especially when the discharge limits for total nitrogen are low.

Life-Cycle Analysis of Organic Carbon Sources

This portion of the report examines alternative carbon sources for denitrification—methanol, ethanol, and acetic acid—using life-cycle assessment (LCA). LCA is a tool that allows for the impacts of a product or process to be compared across different life stages and impact categories. This ensures that the environmental burden is not being shifted from state to state, or location to location, in pursuit of environmental goals, and allows for the overall impact of the product to be examined.

LCA was used to evaluate the following nine impact categories: ozone depletion, global warming, acidification, eutrophication, smog formation, ecotoxicity, particulate respiratory effects, human carcinogenic effects, and human non-carcinogenic effects. All three of the external carbon sources examined for tertiary nitrogen removal are capable of removing nitrogen from wastewater; however, in terms of environmental impact, they are not all the same. In the nine impact categories presented, methanol has the lowest impact in eight of the categories. The exception to this is ozone depletion, where ethanol has the lowest impact. Acetic acid has the greatest impacts in seven of the categories, with the exception of acidification and eutrophication, where ethanol has the highest impact. In terms of relative environmental impact among the three external carbon sources, methanol has the lower impact in most categories, with acetic acid having the greatest impacts.

Methanol Properties and Safety

Methanol (CH3OH) is the simplest aliphatic alcohol, containing a single carbon atom, three hydrogen atoms, and an attached hydroxyl group. Methanol is defined by the U.S. National Fire Protection Association (NFPA) and Occupational Safety and Health Administration (OSHA) as a

Class 1B flammable liquid, or by the United Nations as a flammable liquid (UN Hazard Class 3). It is also toxic to humans and the environment if sufficient exposure and releases occur. Safe storage, handling, and use of methanol are therefore important concerns. However, given that WWTPs use hazardous chemicals, such as chlorine, on a daily basis, one would expect that plant operators could easily handle methanol safely. According to the *Methanol Safe Handling Manual*, only one methanol-related incident occurred at a wastewater treatment facility between 1998 and 2011.

Disclaimer

As part of its commitment to methanol product stewardship, the Methanol Institute engaged Exponent to prepare this Document. Our intention is to improve the awareness of safe and environmentally sound practices for the handling of methanol throughout the global distribution chain. The information, procedures, recommendations, and data presented in this Document are informational only, and the Document is designed to provide general guidance only. The Methanol Institute and the report authors assume no liability whatsoever with respect to the accuracy and completeness of the information, procedures, recommendations, and data presented in this Document and disclaim all liability arising from the use of such information, procedures, recommendations, and data. All users of this Document must still use their own independent judgment and discretion in ensuring that they handle methanol safely and communicate appropriately. In doing so, they must develop the specific systems that best fit their management structure, product lines, location, and other factors that are unique to the user. We encourage the reader to research the local codes and regulations that may be applicable to the handling of flammable and hazardous materials such as methanol. This Document is not a substitute for applicable laws and regulations, nor does it alter the obligation of the user to comply fully with federal, state, and local laws.

1 Nitrogen in the Environment

1.1 Sources of Nitrogen

All life forms on earth have an obligate requirement for nitrogen. For humans, this is about 4300 g/capita/yr, amounting to about 1.4 Tg/yr in the United States, and 28 Tg/yr globally (a teragram is one million metric tons). Although there are vast quantities of diatomic nitrogen in the earth's atmosphere, only a few species of plants, bacteria, and archaea have evolved that are able to convert N_2 into usable forms, a process known as biological nitrogen fixation (BNF). Most other species have been driven to use these limited natural sources as efficiently as possible. Collectively, non-N_2 forms of nitrogen are termed "reactive nitrogen," which will be referred to in this report as Nr. Reactive nitrogen encompasses all biologically active, chemically reactive, and radiatively active nitrogen compounds in the atmosphere and biosphere of earth. Thus, Nr includes inorganic chemically reduced forms of N (e.g., ammonia [NH3] and ammonium ion [NH_4^+]), inorganic chemically oxidized forms of N (e.g., nitrogen oxides [NOx], nitric acid [HNO_3], nitrous oxide [N_2O], N_2O_5, HONO, peroxy acetyl compounds such as PAN, and nitrate ion [NO_3-]), as well as organic compounds (e.g., urea, amines, amino acids, and proteins) (U.S. EPA 2011).

As the human population has grown, there has been a proportional growth in the need for Nr. During the 18th century, this need was met largely through importation of naturally occurring nitrates and bird guano, mostly from the Pacific Islands and South America to Europe. However, near the beginning of the 20th century, such sources were insufficient to meet continually increasing dietary needs. Coincidentally, Haber and Bosch, working in Germany, succeeded in perfecting the catalytic conversion of N_2 into reduced nitrogen (NH3) at low cost, thereby setting in motion a series of industrial expansions (e.g., agriculture, chemicals, armaments) with significant consequences, both positive and negative. The advent of the Haber-Bosch process has been called one of the most important discoveries in human existence, because it uncoupled our need for Nr from natural sources, and resulted in major shifts in the earth's biogeochemical nitrogen cycle (Smil 2001). Significant additional Nr is created through combustion associated with energy production (including power production, industrial boilers, and transportation), and the purposeful planting of legumes such as soybeans. These sources of Nr are sometimes termed "new" reactive nitrogen to distinguish it from pre-human sources. Figure 1-1 provides a breakdown of all sources of Nr in the United States in 2002, the most recent year for which complete data are available. Total U.S. production of Nr is 35 Tg/yr, all but 6.4 of which are human generated. Slightly over half (18.6 Tg/yr) of the "new" Nr comes from agricultural uses; thus, over an order of magnitude of excess Nr is generated to meet the U.S. dietary need. Denitrification, the conversion of oxidized Nr to N_2, is a naturally occurring process that "closes" the nitrogen cycle. The magnitude of denitrification in the U.S. is estimated to be about 16 Tg/yr; thus, Nr continues to accumulate in the environment.

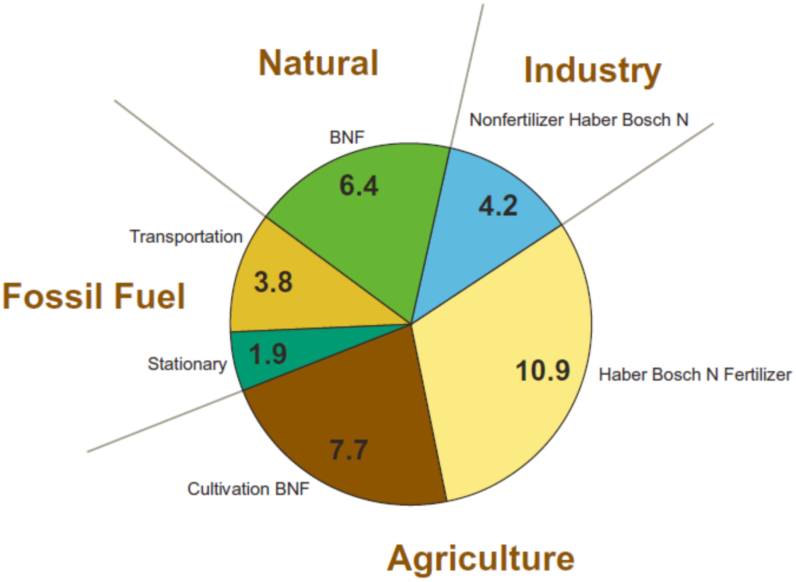

Figure 1-1. Sources of reactive nitrogen (Nr) introduced into the U.S. in 2002 (Tg N/yr) (Source: U.S. EPA 2011).

Virtually all of the Nr produced is eventually released to the environment, where it can undergo a variety of chemical transformations and be translocated to other parts of the biosphere. In each case, the specific form and location of Nr leads to an array of impacts that range from nutrient enrichment, to human toxicity, to ecosystem impairment, to decreases in visibility. Thus, the release of one molecule of Nr to the atmosphere in the form of, say, NO_2 will create a series of air-related impacts and then can be deposited in the terrestrial or aquatic sectors, where conversion to other forms of nitrogen, such as NH_3 or N_2O, will create a series of new impacts, and so forth. These chemical inter-conversions and sectoral translocations have been termed the “nitrogen cascade” (U.S. EPA 2011), which is illustrated in Figure 1-2.

In Figure 1-2, the “new” N box depicts the two primary anthropogenic sources by which Nr originates—energy production and food/fiber/biofuel production—and where they enter the biosphere. Food production includes N fertilizer produced in the U.S., cultivation-induced biological nitrogen fixation (C-BNF) in the U.S., production of animals and crops in the U.S. for human consumption, and imports of N-containing fertilizer, grain, and meat to the U.S. The atmospheric system indicates that tropospheric concentrations of both ozone and particulate matter are increased due to NOx emissions to the atmosphere. The ovals illustrate that the increase in N_2O concentrations, in turn, contributes to the greenhouse effect in the troposphere and to ozone depletion in the stratosphere. Transfers of Nr from the atmospheric system occur by deposition to terrestrial and aquatic sectors of the biosphere.

The terrestrial system depicts that Nr enters agricultural lands via food production, but is also introduced to the entire terrestrial landscape via atmospheric deposition. Within agricultural regions, there is cycling among soils, crops, and animals, and then a transfer of Nr as food to populated regions, from which there are Nr losses (e.g., wastewater, landfills). The ovals showing ecosystem productivity and biogeochemical cycling reflect that Nr is transported and transformed within the terrestrial system, and that, as a consequence, there are significant impacts on ecosystem productivity due to fertilization and acidification, often with resulting losses of biodiversity. Nr is stored in both biomass and soils. Transfers of Nr from this system occur by leaching and runoff of Nr to aquatic ecosystems and by emissions to the atmospheric system as various forms of Nr. There is potential for conversion of Nr to N2 via denitrification in the terrestrial system.

The aquatic system shows that Nr is introduced via leaching and runoff from terrestrial ecosystems and via deposition from atmospheric ecosystems. Enabled by the hydrologic cycle, there are Nr fluxes downstream with ultimate transport to coastal systems. Within the aquatic system, the ovals highlight two significant impacts of waterborne Nr—acidification of freshwaters and eutrophication of coastal waters. Losses of Nr from the aquatic system are primarily via N2O emissions to the atmospheric system, plus conversion of Nr to N2 via denitrification in water and wetlands.

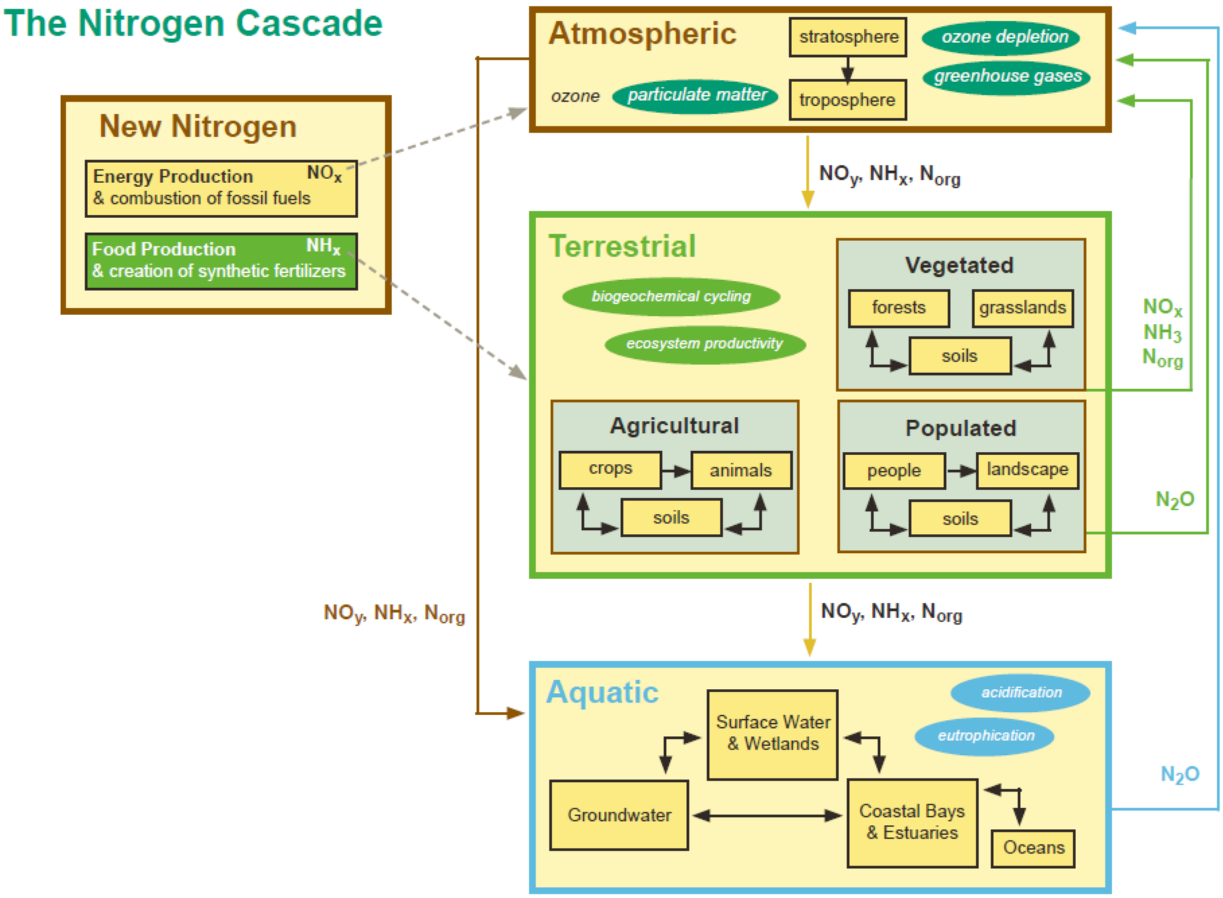

Figure 1-2. The nitrogen cascade (Source: U.S. EPA 2011)

The input of reactive nitrogen to a given system varies considerably by region and source (deposition, manure, artificial fertilizer, and human waste) (van Bremen et al 2002). Such Nr "signatures" illustrate the local character of Nr by source; control strategies for Nr must necessarily be tailored to specific conditions. Thus, while point discharges of Nr from wastewater treatment plants represent a small portion of total Nr in the U.S. (about 1.3 Tg/year), such sources can be important for local water bodies such as pristine lakes and sensitive estuaries and coastal zones.

1.2 Nitrogen Transformations in the Environment

Nitrification is the oxidation of NH_4^+ ion to NO_3^- (Figure 1-3). Most commonly, nitrification is a chemolithotrophic process that consists of the conversion of ammonium to nitrite, which is then converted to NO_3^- by a second group of bacteria. The ammonium oxidizing bacteria (AOB) are obligate aerobes with some species that are tolerant of low-oxygen environments. The most common genera of autotrophic NH_4^+ oxidizers are Nitrosospira and Nitrosomonas, which result in the formation of nitrite. AOB are found in most aerobic environments where ammonium is available through the mineralization of organic matter or N compounds are added.

Biological denitrification is the dissimilatory reduction of NO_3^- and nitrite to produce NO, N_2O, and N_2 by a taxonomically diverse group of bacteria. These bacteria synthesize a series of reductases that enable them to utilize successively more reduced N oxides as electron acceptors in the absence of oxygen. The general reductive sequence is shown in Figure 1-5. In addition to the free-living denitrifiers, symbiotically living Rhizobia in root nodules of legumes are able to denitrify nitrate and produce nitrous oxide (Mosier and Parkin 2007). Denitrifiers are heterotrophs, which require sources of electron-reducing equivalents contained in available organic matter. Factors that most strongly influence denitrification are oxygen, nitrate concentration, pH, temperature, and organic carbon. The reductive enzymes are repressed by oxygen but not by NH_4^+. Nitrous oxide reductase appears to be more sensitive to oxygen than either NO_3^- or nitrite reductase. Therefore, N_2 production predominates in more anoxic sites, and N_2O production may be greater in more aerobic conditions. However, the ratio of N_2 to N_2O emitted may also be affected by high NO_3^- concentrations and associated higher levels of electrical conductivity and osmotic stress and soil pH (low pH favors N_2O production).

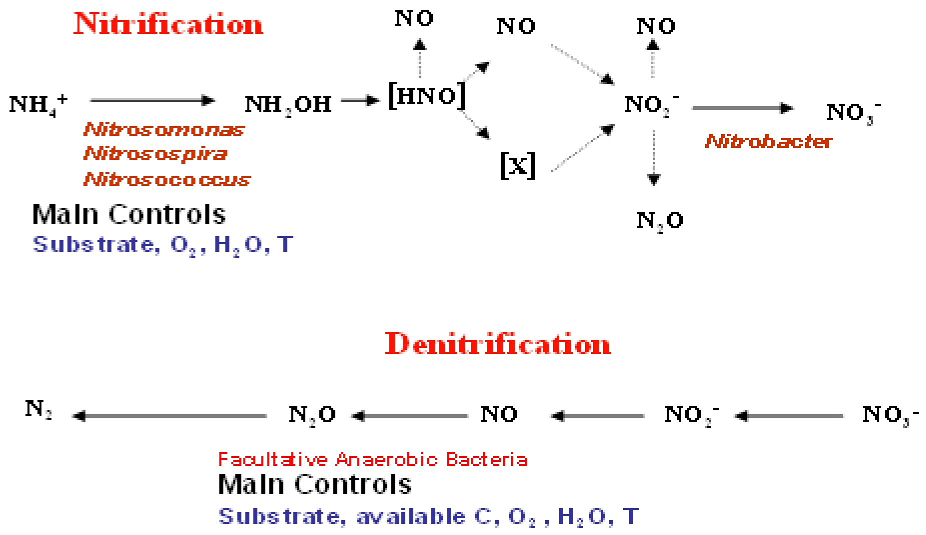

Figure 1-3. Diagram of the nitrification and denitrification processes (from Mosier and Parkin 2007)

1.3 Impacts of Excessive Reactive Nitrogen

Essentially all of the Nr created by human activities is released to the environment, often with unintended negative consequences. It circulates between, and accumulates within, the atmospheric, aquatic, and terrestrial ecosystems. As summarized in Table 1-1, it contributes to a number of adverse public health and environmental effects, including photochemical smog, nitrogen-containing trace gases and aerosols, decreased atmospheric visibility, acidification of terrestrial and aquatic ecosystems, eutrophication of coastal waters (i.e., harmful algal blooms, hypoxia), drinking-water concerns, freshwater Nr imbalances, greenhouse gas (GHG) emissions and subsequent climate change, and stratospheric ozone depletion.

Table 1-1. Examples of impacts of excess reactive nitrogen on human health and environment (from U.S. EPA 2011)

Impact	Cause	Location	Metric	Source	Reference
Acidification of surface waters; loss of biodiversity	Acidification of soils, streams and lakes is caused by atmospheric deposition of sulfur, HNO_3, NH_3, and ammonium compounds.	Primarily mountainous regions of the United States	Out of 1,000 lakes and thousands of miles of streams in the Eastern United States surveyed, 75% of the lakes and 50% of the streams were acidified by acid deposition	Fossil fuel combustion and agriculture	http://www.epa.gov/acidrain
Biodiversity loss	Nitrogen deposition	Grasslands and forests in the United States receiving N deposition in excess of critical load	Decrease in species richness of grasslands and forests	Utilities, traffic, and animal agriculture	Bobbink et al. 2009; Fenn et al. 2003.
Forest decline	Ozone and acid deposition	Eastern and Western United States	Decreased timber growth; increased susceptibility to disease and pests	Utilities, traffic, and animal agriculture	Johnson & Siccama 1983; MacKenzie & El-Ashry 1990
Crop yield loss	Ozone	Eastern and Western United States	$ 2-5 billion/year	Utilities & traffic	Heck et al. 1984
Hypoxia of coastal waters	Excess nutrient loading, eutrophication, variable freshwater runoff	Gulf of Mexico, other estuarine and coastal waters	Benthic finfish/shellfish habitat loss, fish kills, sulfide toxicity, costs >$50 million/year	N, P from energy and food production	Bricker et al. 1999, Verity et al. 2006; U.S. EPA SAB 2008; Rabalais et al. 1999; Mitsch et al. 2001
Harmful Algal Blooms	Excessive nutrient loading, climatic variability	Inland and coastal waters	Fish kills, losses of drinking and recreational waters costs >$100 million/year	Excess nutrient (N & P) loading	Paerl 1988; ECOHAB 1995; NRC 2000
Visibility decrease	Fine particulate matter	National Parks and wilderness areas	visibility impairment	NO_y and NH_x from fossil fuels and agriculture	Malm et al. 2004 EPA-CASAC-09-010
Human mortality	$PM_{2.5}$, O_3 and related toxins.	US urban and nearby areas.	Pollution related deaths estimated at 28,000-55,000 per year. (a range of cardiovascular and respiratory system effects are associated with this pollution)	NOy and NHx from fossil fuels and agriculture	Mokdad et al. 2004; Ezzati et al. 2004
Total damage to public health and environment	NO_x into air	Chesapeake Bay Watershed	$3.4 Billion; 200,000 Mt	Mobile sources	Moomaw and Birch 2005
Total damage to public health and environment	NH_x and nitrate into air and water	Chesapeake Bay Watershed	$1.5 Billion;400,000 Mt	Agriculture	Moomaw and Birch 2005

2 Regulatory Climate for Nitrogen in Wastewater

2.1 Water Quality Regulation and Management in the United States

2.1.1 Aquatic Thresholds

In aquatic ecosystems, thresholds at which excess reactive nitrogen (Nr) becomes a problem can be expressed as a management goal such as a total maximum daily load (TMDL) or as a critical load (CL). A TMDL sets a goal for reducing the load of a specific pollutant that is causing impairment to a water body. Under the authority of the Clean Water Act (CWA), EPA has developed guidance for establishing numeric nutrient criteria on an eco-regional basis for lakes and reservoirs, streams and rivers, estuaries and coastal waters, and wetlands. EPA has proposed specific numbers for lakes and reservoirs and rivers and streams, and protocols for developing criteria for estuaries and wetlands. Each state is advised to go through an assessment to determine the best methodology for implementing numeric criteria (U.S. EPA 2000b,c, 2001, 2007). These criteria are intended to identify impaired water bodies for which TMDLs may be required.

The second type of threshold available for aquatic ecosystems is the critical load (CL). Unlike the TMDL, the CL (in the United States) has no regulatory framework but rather sets the threshold of Nr loading at which negative impacts have been documented. Based extensively on European work, CLs for aquatic ecosystems are Nr inputs on the order of 2–15 kg N/ha/yr (Bobbink et al. 2009). There are numerous locations within the United States where deposition to surface waters falls within this range.

2.1.2 Water Quality Standards

Section 303 of the CWA requires states to adopt water quality standards and criteria that meet the state-identified designated uses (e.g., uses related to “fishable” and “swimmable”) for each water body. Specifically, “A water quality standard defines the water quality goals of a water body, or portion thereof, by designating the use or uses to be made of the water and by setting criteria necessary to protect the uses” (40 CFR Sec. 131.2). Further, “Such standards serve the dual purposes of establishing the water quality goals for a specific water body and serve as the regulatory basis for the establishment of water-quality-based treatment controls and strategies beyond the technology-based levels of treatment required by sections 301(b) and 306 of the Act” (40 CFR Sec. 131.2).

EPA sets minimum requirements for approvable standards and criteria, including use designations, water quality criteria sufficient to protect the designated uses, and an anti-degradation policy (40 CFR Sec. 131.6). Traditionally, Nr and other land, air, and water pollutants are measured in terms of quantity (mass) released per unit time (e.g., kg/day) or as a concentration (e.g., milligrams per liter, hereafter mg/L). Therefore, regulations often specify mass loading limits or maximum concentrations in permits.

In the mid- to late 1990s, EPA began to emphasize the development of numeric nutrient criteria for both phosphorus (P) and Nr through the state standards-setting process. Few states had adopted numeric nutrient criteria for all affected water bodies, especially for Nr, often relying on narrative criteria or secondary effects such as chlorophyll-a concentration, dissolved oxygen, or water clarity. EPA's strategy mandated numeric nutrient criteria to begin to address the problem. To move the objectives of the Clean Water Action Plan forward, EPA published national nutrient criteria guidance for lakes and reservoirs (U.S. EPA 2000b), rivers and streams (U.S. EPA 2000c), estuaries and coastal waters (U.S. EPA 2001), and wetlands (U.S. EPA 2007), based on eco-regional guidance for lakes and reservoirs and rivers and streams. To date, relatively few states have adopted new numeric criteria into their water quality standards. While some successes are evident in promulgating phosphorus criteria for freshwater systems, which has a richer history of numeric criteria incorporation into state water quality standards, development of numeric nitrogen criteria has been elusive for a variety of reasons.

Multimedia and multijurisdictional N management can be complicated, because the CWA has little authority over atmospheric sources, and individual states explicitly lack authority to control upstream sources. Quite often in estuaries, such as the Gulf of Mexico or Chesapeake Bay, management goals that meet water quality standards cannot be attained without interstate compacts or a strong federal role, which may be resisted by upstream states that may have to bear the cost but do not necessarily reap the benefits of the water quality improvement. Such a dilemma underscores the need for an integrated approach to Nr management.

Populated (urban/suburban/developed) land areas provide significant loads of Nr to the environment, both by generation (e.g., deposition of NOx emissions) and by transfer (e.g., domestic sewage from imported food). Categorical sources include sewage treatment plants, industries, subsurface (septic) systems, atmospheric deposition, domestic animal and wildlife waste, and fertilizers used on lawns, gardens and landscapes. Infrastructure (e.g., storm sewers) and landscape conditions (e.g., increased impervious cover) more efficiently move Nr associated with surface runoff to receiving waters and may also inject or infiltrate Nr into groundwater. Landscape changes, primarily increases in impervious cover, soil disturbance and compaction, and wetland/hydric soil losses, have also reduced the capacity for natural systems to treat Nr inputs by recycling or denitrification. Other disruptions in chemical condition (e.g., acidification), biology (e.g., vegetative cover), and physical character (e.g., temperature increase) alter the nitrogen cascade, which may have both negative and positive consequences for Nr amelioration on the populated landscape and in air and water. Populated lands are estimated to export as much as 10 times the total nitrogen that was exported under pre-development conditions (EPA 2011)

2.1.3 Attainment of Water Quality Management Goals and Standards

Estuarine systems, where bioavailable Nr is more likely to be the limiting nutrient, are most often susceptible to Nr enrichment (Paerl 1997; Boesch et al. 2001). Defining single-number criteria for nutrients or related indicators representative of undesirable levels of productivity (e.g., chlorophyll a) is difficult, even using the eco-regional approach recommended by EPA. State managers more often use the formal TMDL process or collaborative estuarine management plans to set site- or estuary-specific N management targets to meet existing, related water quality criteria (e.g., dissolved O_2 or chlorophyll a). Some of the more prominent efforts and targets for nitrogen control are summarized in Table 2-1.

Table 2-1. Estuaries with nitrogen management plans or TMDLs and percent nitrogen load reduction targets

Estuary	Nitrogen Load Reduction Target	TMDL or Plan
Casco Bay, Maine	45%	Plan
Chesapeake Bay	>40%	Plan
Northern Gulf of Mexico Mississippi Plume Region	45%	Plan
Long Island Sound	~60% for CT & NY sources	TMDL
Neuse River Estuary, NC	30%	TMDL
Tampa Bay, FL	Maintain TN load at 1992-1994 levels	TMDL & Plan

The Chesapeake Bay Program, for example, is a model for Nr and P management in many ways. Considerable resources were committed, and many best management practices (BMPs) implemented. Yet, despite regional efforts and commitments from all watershed states, and more funding than any other estuary program is likely to see, management targets have not been met. Concerns over the slow progress in restoring the Chesapeake Bay led to the issuance of an Executive Order on May 15, 2009, establishing a Federal Leadership Committee led by the EPA to develop and implement a plan to restore the Bay in collaboration with state agencies (Federal Register: 74(93):23097–23104).

Another illustrative example is the case of Long Island Sound, where the impairment consists of low concentrations of dissolved oxygen that violate both Connecticut’s and New York’s water quality standards. Nr has been identified as the pollutant that causes substandard levels of dissolved oxygen in Long Island Sound and, accordingly, Connecticut’s and New York’s environmental agencies have developed a TMDL that assigns nitrogen reductions from both point sources (the waste load allocation, or WLA) and nonpoint sources (the load allocation or LA) in their respective states to meet the established 58.5% reduction of anthropogenic sources. The Long Island Sound TMDL is set at 23,966 tons of N/year, which represents a 23,834-ton/year reduction from the total baseline (anthropogenic + natural sources considered) of 47,788 tons/year from Connecticut and New York only. Most of the N load comes from point sources—POTWs (publicly owned treatment works) and CSOs (combined sewer overflows)—accounting for 38,899 tons/yr of the total N load from the two states, or 81% of the load. For that reason, the focus has been on managing point sources, although attainment of water quality standards will require more widespread reductions from atmospheric deposition, stormwater, and nonpoint sources, and from other watershed states north of Connecticut.

2.1.4 Water Quality Monitoring and Assessment

Under Sec. 106 of the CWA, the EPA provides funds to assist state and interstate agencies and tribes in conducting monitoring of the nation's waters to ensure that adopted water quality criteria and designated uses are met. Further, primarily under Sec. 305(b) of the CWA, those entities are required to report, on a biennial basis, the health and status of their jurisdictional waters. These assessments are presented by the states to EPA to categorize attainment of designated uses. EPA published these reports until 1998 (EPA 2000a), after which it transitioned to a Water Quality Report in 2000 (EPA 2002) and a National Assessment Database in 2002 (http://www.epa.gov/waters/305b/index.html). States also prepare a list of "impaired" waters under Sec. 303(d) of the CWA (U.S. EPA 1999). Subsequent reports will provide a synthesis of CWA Sec. 305(b) and 303(d) reporting under a Consolidated Assessment and Listing Methodology, or "CALM," approach.

The EPA compiles the approved state 303(d) lists into a national listing (http://iaspub.epa.gov/waters/national_rept.control). The list provides information by state, as well as by impairment cause, and identifies the TMDLs completed to date. The most current data report available on the EPA web site includes reporting from most entities through 2004. The report identifies 5,617 impairments related to "nutrients" (almost 9% of all identified impairments), although other impairments may ultimately have a nutrient enrichment cause. It should also be clear that impairments may have multiple causes, so for example, waters identified as impaired by oxygen depletion may also be impaired by nutrients. For example, oxygen depletion (4,540), turbidity (2,050), algal growth (510), ammonia (generally toxicity, 416), and hazardous algal blooms (HABS) can all have a common cause such as Nr or P enrichment.

There are other initiatives promoted by EPA to monitor and assess the nation's waters, generally implemented in collaboration with, or by, the state and interstate agencies and tribes that have jurisdiction over the waters. These include the Wadeable Stream Assessment (WSA) (U.S. EPA 2006a), the National Coastal Assessment (NCA) and its National Coastal Condition Reports (U.S. EPA 2001, 2004, 2006b), the Survey of the Nation's Lakes and Survey of the Nation's Rivers and Streams, and more recently, probabilistic monitoring efforts in lakes, streams, and estuaries (http://www.epa.gov/owow/monitoring/reporting.html). Many of these are aimed at including a biological assessment component that is often lacking in water pollutant and chemistry efforts described above.

The National Oceanic and Atmospheric Administration has periodically produced estuarine assessments under the National Estuarine Eutrophication Assessment (NEEA) program. The most recent report was released in 2007 (Bricker et al. 2007). The report has a focus on nutrient enrichment and its manifestations in the estuarine environment and relies on participation and interviews of local experts to provide data for the assessment. Among the key findings were:

- Eutrophication is a widespread problem, with the majority of assessed estuaries showing signs of eutrophication—65% of the assessed systems, representing 78% of assessed estuarine area, had moderate to high overall eutrophic conditions.

- The most common symptoms of eutrophication were high spatial coverage and frequency of elevated chlorophyll a (phytoplankton)—50% of the assessed estuaries, representing 72% of assessed area, had excessive chlorophyll a ratings.

2.1.5 Water Quality Regulation and Management in Europe

The European Union has undertaken broad measures, based on the critical loads concept, to manage Nr. Tables 2-2, 2-3, and 2-4 summarize several different environmental impacts, currently used indicators, and whether there are current limit values set by the United Nations Economic Commission for Europe (UNECE) or European Union (EU). These tables identify the main links to the cascade of reactive nitrogen in the environment, the relevance and link to Nr of the effect/pollutant, and existing agreements in which the effect is currently addressed. In addition, some impacts are more relevant than others in relation to societal importance and the connection to the nitrogen cascade. The categorization on a scale of 1 (highest relevance) to 5 (unimportant) provides a first-level prioritization for future mitigation activity. The last column summarizes existing links to international regulations and conventions.

Where there is a limit and the relevance for the nitrogen cascade is high, this might be the limiting factor for Nr production and its associated losses to the environment. Some limits might be more relevant in specific areas and less relevant in others. For example, NO_2 concentrations relevant for human health are limited to 40 ppb in urban areas, limiting industry and traffic, but are probably not an issue in remote areas with low population densities. In these areas, however, loss of biodiversity might limit nitrogen deposition, and therewith, the sources in the region. The only way to determine the extent that critical thresholds are limiting is by overlaying them for different regions and determining through monitoring data or by model exercises where and which sources contribute to exceeding the critical threshold, and then identifying the best methods for putting caps on relevant sources. A pre-classification of regions might be useful (e.g., urban regions, remote regions, marine areas, etc.).

One aspect of this global view of nitrogen impacts and metrics that is evident is the mix of “classical-” and “service-”based categories, consistent with the need for an integrated approach to the management of nitrogen.

Table 2-2. Summary of the effects of excess Nr on human health in relation to metrics, current international regulations and conventions, and the link to the nitrogen cascade (from U.S. EPA 2011)

Effect	Metrics	Regulated?	Link to Nr Cascade	Relevance*	Regulatory or Political Convention
Respiratory disease in people caused by exposure to high concentrations of:					
Ozone	Sum of ozone over 35 ppb	YES	NOx emissions	3	Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Other photochemical oxidants	Org. NO_3, PAN conc (atm)	NO	NOx emissions	5	Indirectly , Convention on Long-range Transboundary Air Pollution et al.
Fine particulate aerosol	PM_{10}, $PM_{2.5}$ conc (atm)	YES	NOx, NH_3 em	1	Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Direct toxicity of nitrite NO2-	NO_2^- conc	YES	NOx	2	World Health Organization Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Nitrate contamination of drinking water	NO_3^- conc (aq.)	YES	NO_3- leaching	2	EU Essential Facilities Doctrine
Depletion of stratospheric ozone	NOx, N_2O conc/flux (atm)	NO	NOx, N_2O	3	Montreal Protocol
Increased allergenic pollen production, and several parasitic and infectious human diseases		NO		5	None
Blooms of toxic algae and decreased swimability of in-shore water bodies	Chlorophyll a NO_3- (&P) conc (aq)	NO	Runoff, Nr deposition	1	Convention for the Protection of the Marine Environment of the North-East Atlantic Helsinki Commission Barcelona Convention

*Relevance and link to nitrogen incorporates societal priority and N contribution: 1) highest relevance, 2) high relevance, 3) significant relevance, 4) some relevance, 5) unimportant.

Table 2-3. Summary of the effects of excess Nr on ecosystems related to currently used metrics, the existence of European regulatory values, and the link to the nitrogen cascade (from U.S. EPA 2011)

	Metrics	Regulated?	Link to Nr Cascade	Relevance*	Regulatory or Political Convention
Ozone damage to crops, forests, and natural ecosystems	AFstY (O_3 flux), AOT40	YES	NO_x	2	Convention on Long-rang**e** Transboundary Air Pollution Clean Air for Europe
Acidification effects on terrestrial ecosystems, groundwaters, and aquatic ecosystems	Critical loads	YES	Nr deposition	2	Convention on Long-rang**e** Transboundary Air Pollution Clean Air for Europe WFD
Eutrophication of freshwaters, lakes (incl. biodiversity)	Biological oxygen demand, NO_3^- conc (aq) Critical loads	YES NO	Runoff, Nr deposition	3	Water Framework Directive
Eutrophication of coastal ecosystems inducing hypoxia (incl. biodiversity)	BOD, NO_3^- conc (aq) Critical loads	BOD, NO_3^- conc (aq) Critical load	Runoff, Nr deposition	1	Convention for the Protection of the Marine Environment of the North-East Atlantic Helsinki Commission Barcelona Convention
Nitrogen saturation of soils (incl. effects on GHG balance)	Critical loads	YES	Nr deposition	1	Convention on Long-rang**e** Transboundary Air Pollution Clean Air for Europe
Biodiversity impacts on terrestrial ecosystems (incl. pests and diseases)	Critical loads, critical levels (NH_3, NOx)	YES	Nr deposition	1	Convention on Long-rang**e** Transboundary Air Pollution Clean Air for Europe, Convention on Biological Diversity

*Relevance and link to nitrogen incorporates societal priority and N contribution: 1) highest relevance, 2) high relevance, 3) significant relevance, 4) some relevance, 5) unimportant.

Table 2-4. Summary of the effects of excess N on other societal values in relation to metrics and regulatory values in current international regulations and conventions and the link to the nitrogen cascade (from U.S. EPA 2011)

	Metrics	Regulated?	Link to Nr cascade	Relevance*	Regulatory or political convention
Odor problems associated with animal agriculture	Acidity in precipitation, O_3, PM	YES	NO_x, NH_3	3	Convention on Long-rang**e** Transboundary Air Pollution
Effects on monuments and engineering materials	$PM_{2.5}$ conc (atm)	NO	NO_x, NH_3	4	
Global climate warming induced by excess nitrogen	N_2O, conc/flux (atm)	NO	NO_x, NH_3	1	United Nations Framework Convention on Climate Change
Regional climate cooling induced by aerosol)	$PM_{2.5}$ conc (atm)	NO	NO_x, NH_3	1	United Nations Framework Convention on Climate Change

*Relevance and link to nitrogen incorporates societal priority and N contribution: 1) highest relevance, 2) high relevance, 3) significant relevance, 4) some relevance, 5) unimportant

The European Water Framework Directive (EU WFD) marked a shift in focus, from point-source control to an integrated prevention and control approach at the water-body level (Benedetti 2006). Tertiary wastewater treatment has increased since 1990, although the percentage of wastewater treatment plants with tertiary treatment varies by region (Figure 2-1) (European Environment Agency, retrieved 2012). This increasing trend in the use of tertiary wastewater treatment coupled with the more stringent treatment objectives, suggests that this will be an expanding market. The EU WFD caused the discharge standards for nitrogen in water to decrease from 10 mg/L to 2.2 mg/L (Wageningen University, retrieved 2012). The goal of this action is to "promote sustainable water use, protect the aquatic environment, improve the status of aquatic ecosystems, mitigate the effects of floods and droughts, and reduce pollution" (Zalewski 2011). Part of the two- step strategy to achieve the directive's goals is the adoption of new wastewater treatment technologies.

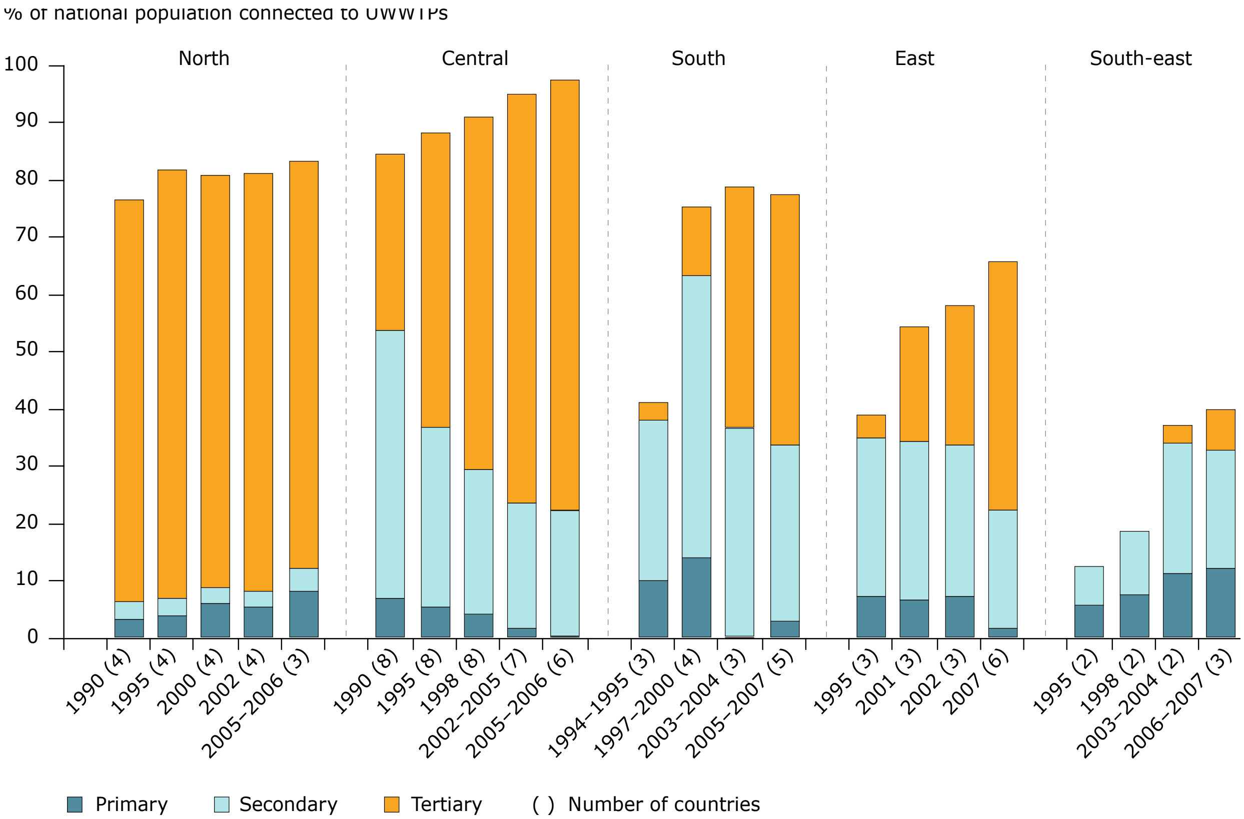

Figure 2-1. Changes in European wastewater treatment from 1990 through 2007 (European Environment Agency, retrieved 2012)

Biological nitrogen removal is being practiced at wastewater treatment plants in Europe, and Europe represents a potentially viable market for the use of methanol in wastewater denitrification. Delfland, located in the Netherlands, is home to one of the largest wastewater treatment plants in Europe (Wouter and de Been, retrieved 2012). By utilizing a methanol-enhanced biofilter for tertiary nitrogen treatment, nitrogen removal down to 0–3 mg N/L was achieved.

Europe’s largest and oldest wastewater treatment plant is located in France, near Paris (Wiseman 2006). The upgrades to the wastewater treatment plant, projected to be completed in 2015, include a fixed-film bio-filter for nitrification and some denitrification, with complete denitrification being completed by a complementary process. The Seine Center wastewater treatment plant, located in Colombes, uses methanol as a tertiary carbon source during wastewater treatment (Tallee et al. 2006; Sewage Treatment in the Greater Paris Area 2006). Methanol is added during denitrification, and the dosing of methanol in part determines the quantity of nitrogen dioxide emissions produced during denitrification. Nitrogen dioxide is an intermediary in the denitrification process, whereby the nitrogen is transformed into nitrogen gas. When denitrification of 66%–88% is achieved, the nitrous oxide emissions are at the highest. However, when 100% denitrification is achieved, the nitrous oxide emissions are at their lowest, representing about 0.2% of the nitrate removed from the wastewater.

2.2 Water Quality Regulation and Management in China

In the past 10–15 years, China has experienced rapid industrialization. With that industrialization comes the need for wastewater discharge standards and more effective wastewater treatment. As of 2002, 35.5% of rivers in China were not suitable for drinking-water use due to pollution issues, which has led to a water shortage in some portions of the country (U.S. Department of Commerce 2005). Environmental legislation put in place in 2003 sets Class 1A effluent discharge standards at <5 mg/L ammonia nitrogen and <15 mg/L total nitrogen (Severn Trent Services 2012) (Table 2-5). As of 2002, only 39% of wastewater in China was being treated; this, coupled with the new legislation, suggests that this is an emerging market for tertiary wastewater treatment for nitrogen removal (U.S. Department of Commerce 2005). The number grew officially to 59% as of 2008 (Innovation Center Denmark, Shanghai, 2009). As of 2005, 60% of cities in China had wastewater utility companies (Browder 2007). As of 2004, in a comparison of wastewater infrastructure among four countries, China's percentage of wastewater treatment coverage in urban areas was greater than that of Brazil, but still lagged behind other developed European countries (Table 2-6) (Browder 2007). In 2007, 55.68 billion cubic meters of wastewater were discharged in China (Innovation Center Denmark, Shanghai, 2009), composed of 44.3% industrial wastewater and 55.7% household and service-sector wastewater. A further breakdown of wastewater treatment in China can be seen in Table 2-7. Due to land constraints, biological removal of nitrogen is an attractive option, often requiring an external carbon source such as methanol (Severn Trent Services 2012). Although some information is available about wastewater treatment and use in China, there is also a documented lack of transparency in the wastewater treatment market (Browder 2007).

Table 2-5. China's wastewater treatment classes
(Wang and Huppes, retrieved 2012; Browder 2007

Parameter (mg/L)	Class 1A (Grade 1 Standard A)	Class 1B (Grade 1 Standard B)	Class 2 (Grade 2 Standard)	Class 3 (Grade 3 Standard)	Input Wastewater
COD	50	60	100	1201	146-293
BOD5	10	20	30	601	44.7-181
SST	10	20	30	50	
TN	15	20	-	-	20.3-37.3
NH3-N	5	8	25	-	16.3-33.8
TP	0.5	1	3	5	2.4-4.9

Table 2-6. International performance comparisons
(Browder 2007)

Key Indicators	China	Brazil	Russia	United Kingdom
Water coverage in urban areas (%)	86	81	99	100
Wastewater coverage in urban areas (%)	43	38	90	100
Population per km of distribution network	1100	357	400	>200
Water metering (% of connected population metered)	90	88	<30	<50
Domestic water tariff ($/m3)	$0.15-$0.30	$0.65-$0.80	$0.35-$0.45	$2.20-$2.70
Water production (liters per capital/day)	303	274	450	300
Domestic water consumption supplied by municipal utilities (%)	46	71	68	80
Total average non-revenue water (%)	18	46	40	15
Total average non-revenue water (m3/km network a day)	54	42.3	20	5
Operating cost coverage ratio	1.0	1.0	1.0	1.2
Payment collection rate (%)	85	94	90	99.5

Sources: Prepared by Alexander Danilenko (2006), World Bank. Chinese data based on Chinese Water Works Association Yearbook (2005); UK data on OFWAT annual performance report (2005); Brazil on SNIS (2006); Russian data on Goskomstate(2006); and World Bank estimates.

Table 2-7. Wastewater discharge and treatment (2001–2007)
(Innovation Center Denmark, Shanghai, 2009)

Item	2000	2001	2004	2005	2006	2007
Wastewater discharge (100 million tons)	415.2	432.9	482.4	524.5	536.8	556.8
Industrial discharge	194.2	202.6	221.1	243.1	240.2	246.6
Direct discharge into seas	8.2	8.6	14.1	15.2	13.2	15.7
Household and service discharge	220.9	230.2	261.3	281.4	296.6	310.2
COD discharge (10,000 tons)	1445.0	1404.8	1339.2	1414.2	1428.2	1381.8
Industrial discharge	704.5	607.5	509.7	554.7	541.5	511.1
Household and service discharge	740.5	797.3	829.5	859.4	886.7	870.8
Ammonia nitrogen discharge (10,000 tons)		125.2	133.0	149.8	141.4	132.3
Industrial discharge		41.3	42.2	52.5	42.5	34.1
Household and service discharge		83.9	90.8	97.3	98.9	98.3
Proportion of industrial wastewater meeting discharge standards (%)	76.9	85.2	90.7	91.2	90.7	91.7
COD removed from industrial wastewater (10,000 tons)	819.8	1045.8	1043.9	1088.3	1099.3	1265.4
Ammonia removed from industrial wastewater (10,000 tons)		34.1	46.6	48.3	55.3	51.8
Facilities of wastewater treatment	64,453	61,226	66,252	69,231	75,830	78,210
Annual expenditure for operation (100 million RMB)	132.5	195.8	244.6	276.7	388.5	428.0

Many forces are at play in expanding China’s water infrastructure (Browder, 2007). The four top driving factors are:

- Rapidly growing urban population
- Backlog of infrastructure improvements, many of which have been deferred from the time before China’s economy experienced rapid growth
- The Chinese government’s expansionary fiscal policy
- A recognition that infrastructure is necessary for economic development.

The Jiashan City wastewater treatment plant, located in the Zhejang province, includes a pilot-scale setup for nitrogen removal (Severn Trent Services 2012). This is a three-stage fixed-film biological nutrient removal process that uses an external carbon source for denitrification. External carbon sources for nitrogen removal have been studied in terms of their effect on the rate of nitrogen removal (Yong-zhen, Yong, & Shu-ying, 2007). The addition of methanol, ethanol, or acetate as an external carbon source was found to increase the potential and rate of denitrification when compared with the wastewater itself.

Other wastewater treatment plants in China treat to the 1A standard for discharge (Kardan Water). Three wastewater treatment plants in Tianjin City treat a combined 130,000 cubic meters of wastewater per day. Two of the plants are currently treating to a 1A standard, while a third is being upgraded from 1B to 1A in 2012. Four wastewater treatment plants in Zibo City treat to the 1A standard, with a combined capacity of 130,000 cubic meters per day. One plant in Zhangjakou City treats 120,000 tons of wastewater per day to the 1A level, and provides water reuse of 30,000 tons per day to the neighboring area.

Between 2002 and 2013, approximately $22 billion has been budgeted to be spent on water and wastewater treatment infrastructure upgrades (U.S. Department of Commerce 2005). According to this source, domestic wastewater treatment technology has a competitive advantage when it comes to price over foreign wastewater treatment technology. A benefit to the United States is that products and technology manufactured in the United States are seen as being of high quality. The list (Table 2-9) of the best potential market in China for the United States, in terms of wastewater treatment technology, included the need for “Biological denitrification and phosphorus-removal technology with high-efficiency and energy-saving technologies.”

Table 2-8. China's wastewater technology needs
(U.S. Department of Commerce 2005)

Technology Needs with the Most Opportunity
Biological denitrification and phosphorus removal technologies
Membrane separation and manufacturing technologies and equipment
Manufacturing technology of anoxic biological reactors
High-concentration organic wastewater treatment technology and equipment
Series-standard water and wastewater treatment equipment with high efficiency
Water-saving technologies and equipment
Water treatment agents
Monitoring instruments
Natural water-body rehabilitation technology

3 Biochemistry of Biological Nitrogen Removal

3.1 Nitrogen in Wastewater

Urea, fecal matter, and food processing wastes are the primary sources of nitrogen for municipal wastewater. Domestic wastewater typically has a total nitrogen content that is about one-fifth of the biochemical oxygen demand (BOD), with typical nitrogen concentrations ranging from 20 to 70 mg/L. About 60% to 70% is ammonia-nitrogen, and 30% to 40% percent is organic nitrogen, with less than 1% nitrite and nitrate nitrogen (Tchobanoglous et al. 2003).

The removal of nitrogen in biological treatment systems consists of four basic steps. The first step is the conversion of organic nitrogen to ammonia in a process called ammonification.

$$RNH_2 + H_20 + H^+ \rightarrow ROH + NH_4^+$$

Ammonia is then converted to nitrate in a two-step process called nitrification—the conversion of ammonia to nitrite followed by the conversion of nitrite to nitrate.

$$2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 4\ H^+\ 2\ H_2O$$
$$2\ NO_2^- + O_2 \rightarrow 2\ NO_3^-$$

Finally, nitrate is converted to nitrogen gas by the process of denitrification.

$$NO_3^- + \text{Organic Carbon} \rightarrow N_2 + CO_2 + H_2O + OH^-$$

The processes of nitrification and denitrification are discussed in greater detail in the following sections.

3.2 Nitrification

Biological nitrification is carried out under aerobic conditions by two principal genera of oxidizing bacteria. *Nitrosomonas* convert ammonia to nitrite, and *Nitrobacter* convert nitrite to nitrate. Both types of bacteria are referred to as aerobic chemoautotrophs, because they require oxygen, they derive energy from the oxidation of an inorganic compound (ammonia or nitrite), and they use inorganic carbon dioxide, rather than organic carbon, for cell synthesis.

The overall oxidation reaction for nitrification can be written to include the consumption of carbonate alkalinity, as follows:

$$NH_4^+ + 2\ O_2 + 2\ HCO_3\text{-} \rightarrow NO_3^- + 2\ CO_2 + 3\ H_2O$$

Using the empirical formula for bacteria as $C_5H_7NO_2$, and incorporating both oxidation and cell synthesis reactions, yields the overall nitrification reaction:

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- \rightarrow 0.021\ C_5H_7NO_2 + 0.98\ NO_3^- + 1.88\ H_2CO_3 + 1.04\ H_2O$$

Based on this equation, for every gram of ammonia nitrogen converted to nitrate, 4.2 grams of oxygen and 7.1 grams of alkalinity as $CaCO_3$ are consumed, and 0.17 grams of new cells are formed. The consumption of alkalinity can have deleterious effects on the nitrification of wastewater by lowering the pH of the system, especially at pH values below 6.8. While the optimal removal rate is found in the 7.5 to 8.0 pH range, systems can operate effectively in the 7.0 to 7.2 range. For treatment plants with low incoming alkalinity, the addition of some form of alkalinity, such as sodium bicarbonate or carbonate, may be required to maintain a favorable pH.

3.3 Denitrification

Biological denitrification is carried out under anoxic conditions by a broad range of heterotrophic bacteria through the process of nitrate dissimilation, in which nitrite and/or nitrate are used as the electron acceptor rather than oxygen. Because these organisms can use either oxygen or oxidized nitrogen while oxidizing organic material, these bacteria are referred to as facultative heterotrophs.

Because denitrification is often carried out after most of the organic matter has been consumed aerobically, it is often necessary to add an organic carbon source. The dissimilation reactions for denitrification can be written to include the use of several common organic substrates, as follows:

Methanol:

$$5\ CH_3OH + 6\ NO_3^- \rightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^-$$

Ethanol:

$$5\ CH_3CH_2OH + 12\ NO_3^- \rightarrow 6\ N_2 + 10\ CO_2 + 9\ H_2O + 12\ OH^-$$

Acetic Acid:

$$5\ CH_3COOH + 8\ NO_3^- \rightarrow 4\ N_2 + 10\ CO_2 + 7\ H_2O + 8\ OH^-$$

Using the empirical formula for bacteria as $C_5H_7NO_2$, and incorporating both dissimilation and cell synthesis reactions, yields the overall nitrification reaction when methanol is the carbon source:

$$NO_3^- + 1.08\ CH_3OH + 0.24\ H_2CO_3 \rightarrow 0.056\ C_5H_7NO_2 + 0.47\ N_2 + HCO_3^- + 1.68\ H_2O$$

Based on this equation, for every gram of nitrate nitrogen converted to nitrogen gas, 2.9 grams of methanol are required, 3.6 grams of alkalinity as $CaCO_3$ are produced, and 0.45 grams of new cells are formed. Unlike nitrification, denitrification can raise the pH. However, the effect is usually small, negating the need for pH control. The optimal denitrification rate is found in the 7.0 to 7.5 pH range.

The presence of oxygen will tend to inhibit denitrification by suppressing the nitrate-reducing enzyme production in the facultative heterotrophs. Thus, biological denitrification needs to be carried out in the absence of oxygen to be most effective.

4 Nitrogen Biological Removal Systems

In the past, wastewater treatment was focused on removing solids, measured as total suspended solids (TSS) and organics, measured as biochemical oxygen demand (BOD). The main objective was to prevent the depletion of oxygen because of the degradation of organics in water bodies receiving the treated wastewater. Over time, it became apparent that macronutrients—nitrogen and phosphorus—were the major cause of eutrophication in surface waters. Focus shifted to including nutrient removal at wastewater treatment plants, especially where eutrophication was a major concern.

The Clean Watersheds Needs Survey 2008 Report to Congress (EPA 2008) indicates that, of 17,749 treatment facilities, 848 (5%) currently treat their effluent for nitrogen removal, and an additional 595 (3%) are projected to need nitrogen removal treatment.[1]

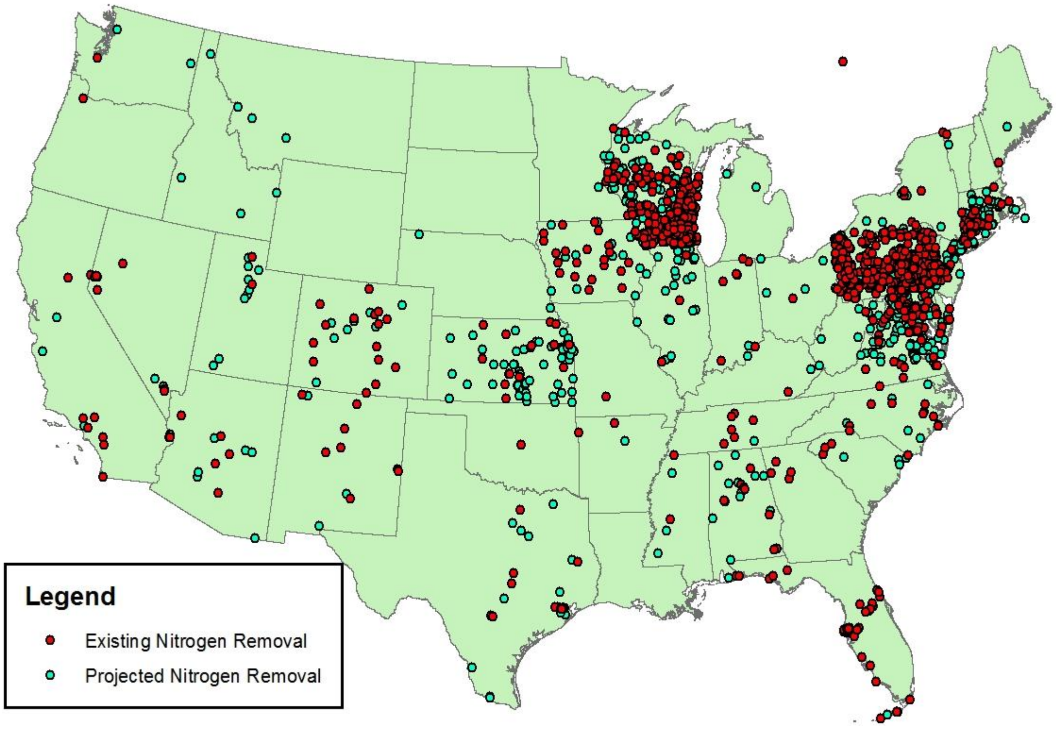

Figure 4-1. Existing and projected N removal for U.S. WWTPs (per CWNS 2008 database)

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[1] The CWNS collected data from over 34,000 wastewater facilities and water quality projects. The data collected included indications of the current and projected treatment needs for the effluent from the treatment facilities. It also includes information about the types of advanced treatment being used.

The CWNS (EPA 2008) provides more detailed information for 284 facilities with denitrification—most (74%) employ activated sludge systems with biological denitrification; separate-stage and filter-based denitrification makes up the remainder. (The Report does not indicate methanol use.)

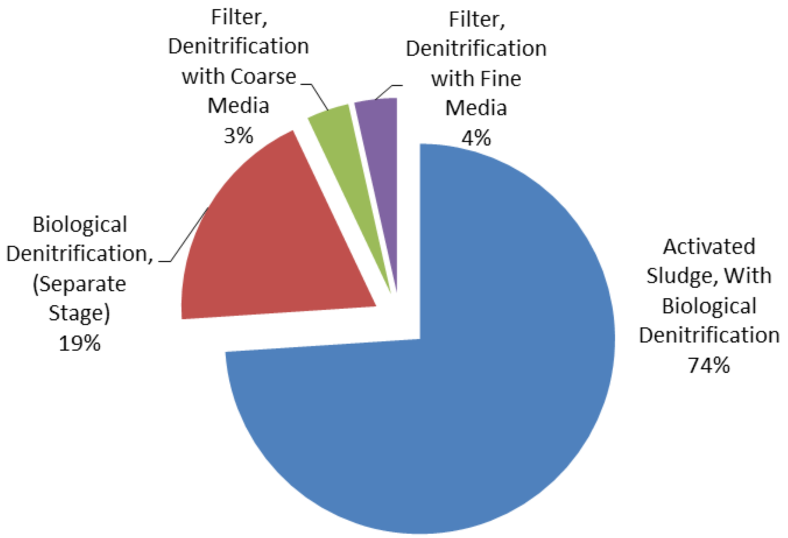


Figure 4-2. Breakdown of N removal technology for U.S. WWTPs (per CWNS 2008 database)

Biological removal of nitrogen can be carried out using various treatment configurations. It can be done using a single-unit process with various treatment zones or in separate stages. Suspended growth, fixed growth, or combined systems can be used. Whatever the treatment system used, they all require an aerobic zone for converting ammonia to nitrate and an anoxic zone for converting the nitrate to nitrogen gas. While there are dozens of nitrogen treatment systems in use, several of the more common configurations reviewed by the EPA are discussed below.

4.1 Single-Process Nitrification/Denitrification

Single-process systems are characterized by alternating between aerobic and anoxic conditions, with only one sludge recycling process.

4.1.1 Modified Luck-Ettinger Process

The Modified-Luck Ettinger (MLE) process is one of the more common treatment systems due to its relative simplicity and use in retrofitting existing secondary wastewater treatment plants. Retrofitting requires additional piping and pumps, along with some form of divider for the treatment zones. The MLE process has two zones: an anoxic zone where nitrate generated in the aerobic zone is reduced to nitrogen gas, and an aerobic zone where BOD removal and nitrification occur, along with air stripping of the nitrogen gas from the anoxic zone. This process has several inherent problems, including high return activated sludge (RAS) and recycle requirements, recycling of dissolved oxygen (DO) from the aerobic tank, and the inability to meet stringent effluent concentrations for total nitrogen due to some of the nitrate being discharged from the aerobic zone. It often requires a supplemental carbon source, such as methanol, to maintain denitrification.

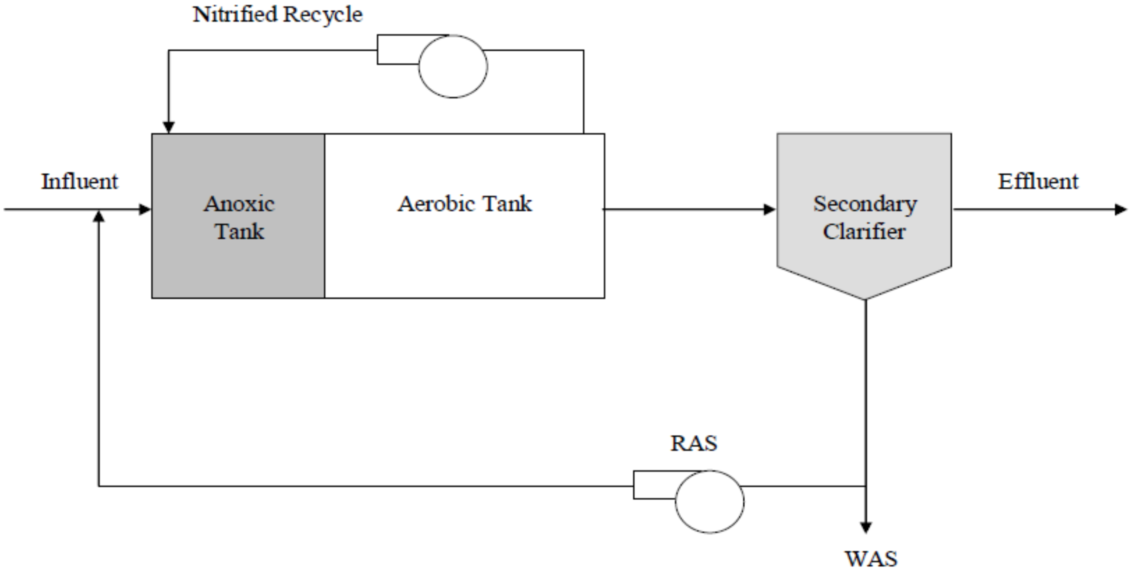


Figure 4-3. Modified Luck-Ettinger process

4.1.2 Four-Stage Bardenpho Process

The Four-Stage Bardenpho process solves some of the problems of the MLE system by adding two additional stages. The third stage is a second anoxic zone where the nitrate leaving the first aerobic tank can be removed by denitrification. This is followed by an aerobic fourth stage where the nitrogen gas is stripped out and the DO increased to improve settling of the sludge in the clarifier. The addition of the extra stages tends to result in lower total nitrogen effluent concentrations than the MLE process. It is often necessary to provide an external carbon source, because most influent organic carbon is consumed in the first aerobic zone.

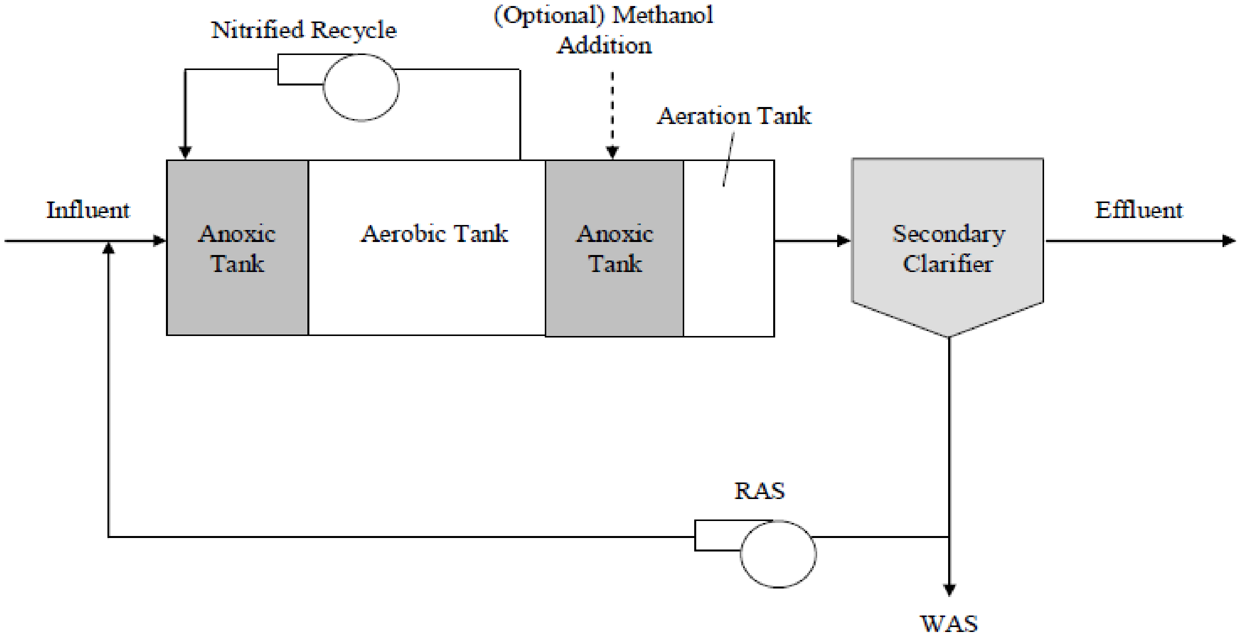


Figure 4-4. Four-Stage Bardenpho process

4.1.3 Sequencing Batch Reactor Process

The sequencing batch reactor (SBR) process is designed to enable all treatment to occur in one tank. Several steps are involved. First, the tank is filled. Second, air and mixing are supplied for BOD removal and nitrification. Third, the air is turned off while mixing continues for denitrification. Fourth, the mixing is turned off to allow the sludge to settle. Finally, the treated liquid is decanted for discharge, and some of the settled sludge is wasted. Then the sequence starts all over again. In order to treat a continuous wastewater flow, it is necessary to have other tanks, with three tanks usually the optimum. While the system can be operated to achieve the desired discharge requirements, the SBR process is best suited to small communities. Depending on the wastewater composition, a supplemental carbon source may be needed.

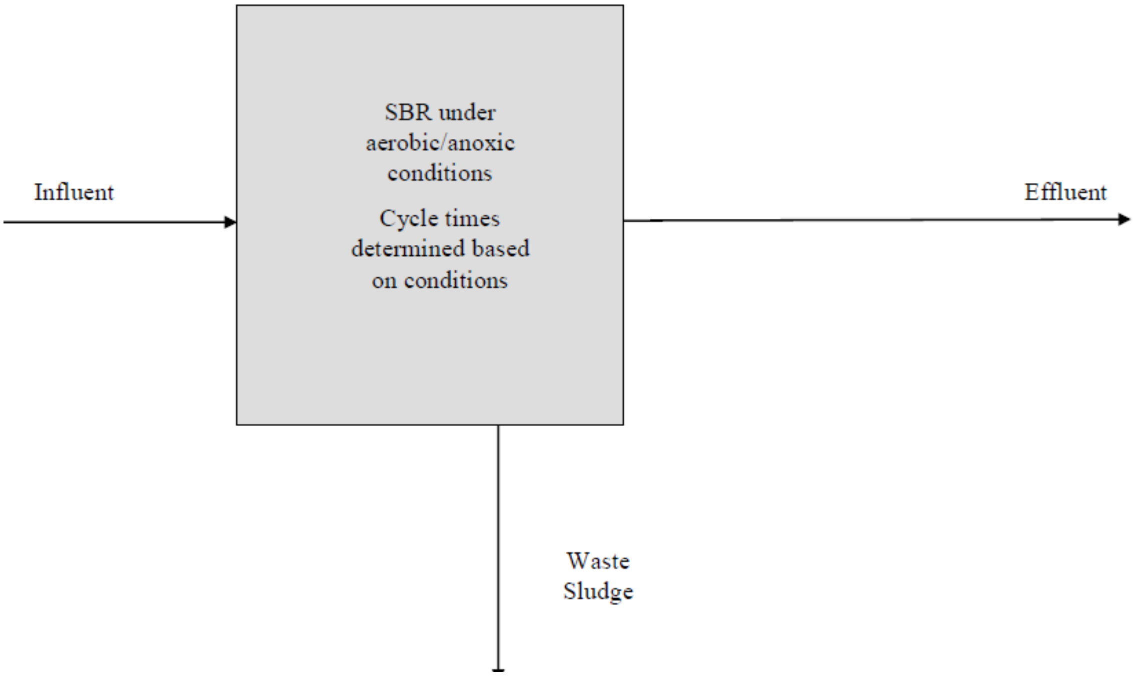


Figure 4-5. Sequencing batch reactor

4.1.4 Step-Feed Process

The Step-Feed Process is based on the desire to eliminate the need for a supplemental carbon source. The wastewater influent is directed into the anoxic zones directly, with lower flow rates introduced in the last unit. One of the advantages of the system is the ability to provide some treatment to wet-weather flows. The excess flow is sent to the last anoxic unit to provide some level of treatment, rather than bypassing the treatment plant. As with the MLE process, it is usually difficult to meet more stringent effluent limits for nitrogen, because some of the wastewater is going directly to the last set of treatment units.

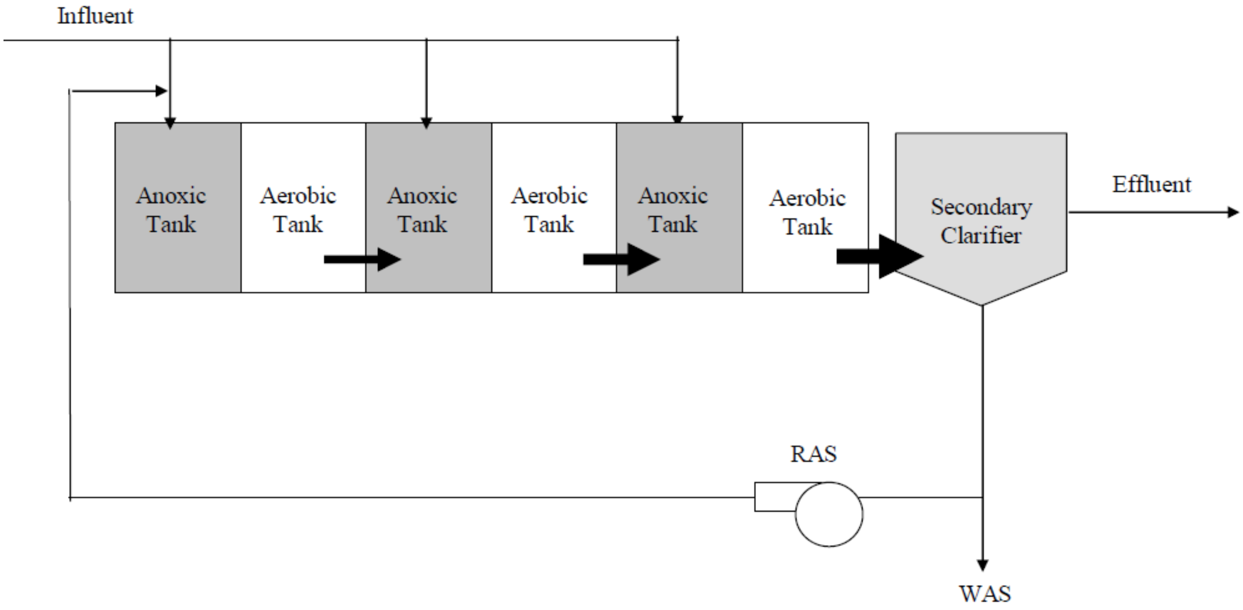


Figure 4-6. Step feed process

4.2 Separate-Stage Nitrification/Denitrification

Separate-stage process systems are characterized by separate treatment units for nitrification and denitrification.

4.2.1 Nitrification Processes

Nitrification is usually carried out in the same treatment unit as BOD removal. However, because of the slower growth rate of nitrifying bacteria, nitrification requires two modifications to conventional activated sludge treatment systems. To maintain a sufficiently high level of nitrifying bacteria, the solids retention time (SRT) must be increased. In addition, the hydraulic retention time (HRT) must be increased to allow for the fact that nitrifiers have a much slower substrate utilization rate than heterotrophs. Based on a comparison of the designs for a conventional activated sludge unit and one incorporating nitrification, Tchobanoglous et al. (2003) showed an increase in the SRT from 5.0 to 12.5 days and an increase in the HRT from 4.3 to 9.0 hours, resulting in a doubling of the required tank volume.

4.3 Denitrification Processes

Separate-stage denitrification can be carried out either as a suspended or attached growth process, both of which require an external carbon source, such as methanol. Because they require a large area and their own sludge settling and recycling system, separate suspended growth denitrification systems are not very common.

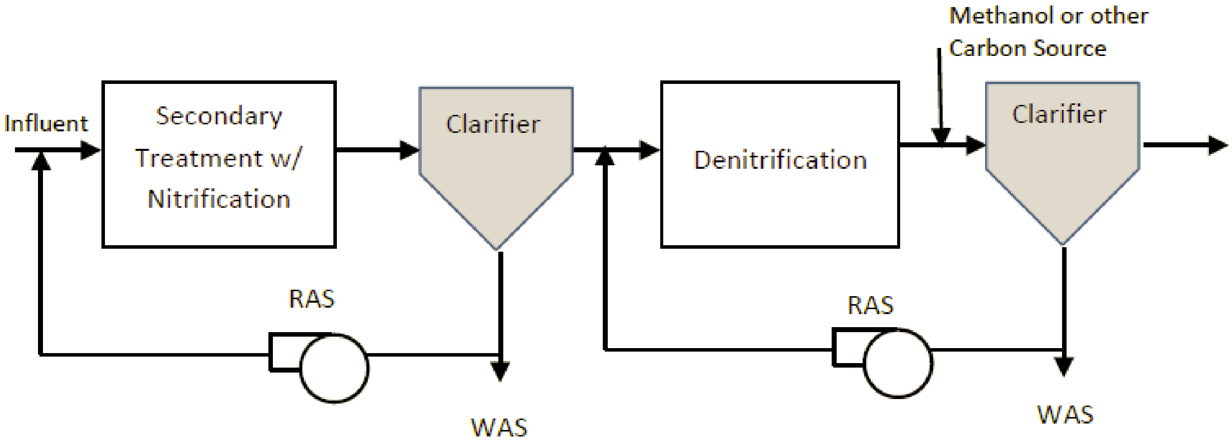


Figure 4-7. Separate-stage suspended growth denitrification process

Denitrification filters are popular, because they are an easy retrofit and require less area and sludge handling. The units can simply be added to the end of a secondary treatment process that includes nitrification. Both downflow and upflow filters are in use. Downflow filters require backwashing to remove solids and nitrogen gas trapped in the filter media. Upflow filters skirt this problem by having the filter media continuously removed from the bottom of the unit, cleaned, and recycled to the top of the filter.

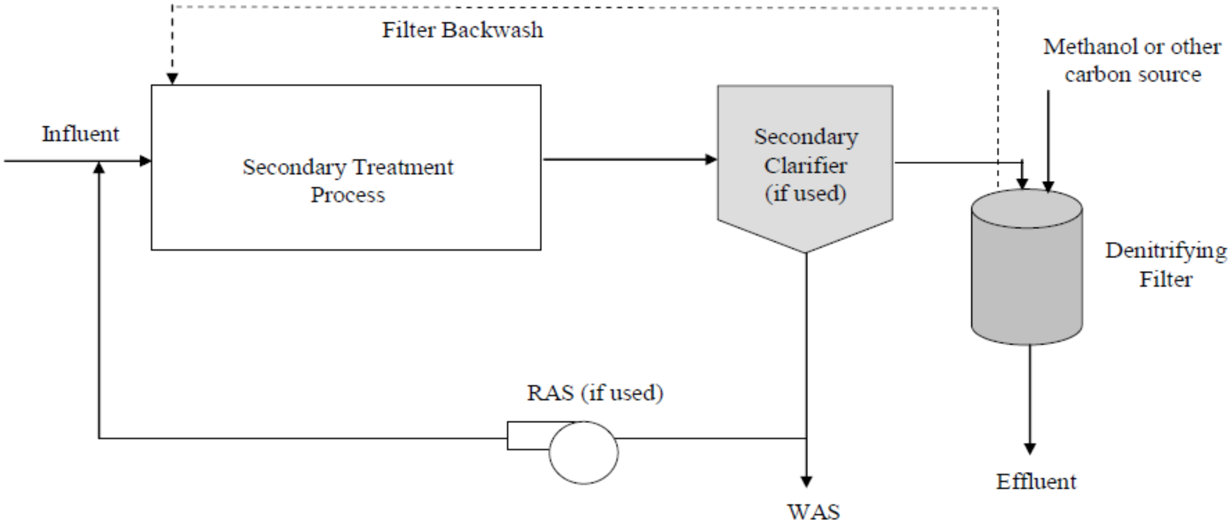


Figure 4-8. Separate-stage denitrification filter process

4.4 History of Success—Case Studies

This section describes the use of methanol in the denitrification process at several wastewater treatment plants around the world.

4.4.1 Western Branch, Upper Marlboro, Maryland

Located in Upper Marlboro, Maryland, the Western Branch Wastewater Treatment Plant (WWTP) was expanded in the early 1990s to include biological denitrification in an effort to minimize nitrogen impacts to the Chesapeake Bay. While permitted for 30 million gallons per day (MGD), the plant treated an average of 19.3 MGD in 2006 (U.S. EPA 2008).

Figure 4-9. Western Branch WWTP. Source: Google Earth. Date of image: 08/28/2012

As one of the first full-scale plants to use denitrification, the plant is unusual, in that it has three separate activated-sludge systems: a high-rate activated sludge system for BOD removal, a nitrification activated sludge system for conversion of ammonia nitrogen to nitrate, and a denitrification activated sludge system for conversion of nitrate to nitrogen gas. Each system has its own treatment basin and clarifier, with internal sludge recycling. Air-stripping channels precede the final clarifiers to remove the nitrogen gas, enabling better sludge settling. Alum is added prior to gravity filtration to remove phosphorus. While permitted to discharge an annual average of 4.0 mg-N/L, the plant averaged 1.63 mg-N/L in 2006, which was the lowest total nitrogen value for any of the seven low-nitrogen plants (<3.0 mg-N/L) evaluated by EPA in

2006 (U.S. EPA 2008). About 2.5 pounds of methanol were added per pound of nitrate-nitrogen entering the denitrification system.

4.4.2 Fiesta Village Advanced, Lee County, Florida

Located in Lee County, Florida, the Fiesta Village Advanced WWTP was upgraded in 1984 to include denitrification. While permitted for 5 MGD, the plant treated an average of 3.2 MGD in 2006 (U.S. EPA 2008). Of the treated effluent, 2 MGD is sent for reuse at golf courses and greenbelts, and the remainder discharges to the Caloosahatchee River.

Figure 4-10. Fiesta Village Advanced WWTP. Source: Google Earth. Date of image: 04/01/2010

The plant consists of an oval extended aeration ditch, followed by clarifiers for sludge settling, downflow denitrification filters, and aeration for nitrogen gas removal. By periodically shutting down some of the brush aerators in the oxidation ditch to create anoxic zones, the nitrate levels are reduced to 3.0 to 3.5 mg/L. After clarification, the flow goes to the denitrification filters, where methanol is added to further reduce total nitrogen to less than 2.0 mg/L. An aeration system is used to strip nitrogen gas prior to chlorination and discharge. Alum is added prior to the clarifiers to remove phosphorus. While permitted to discharge an annual average of 3.0 mg/L-N, the plant averaged 1.71 mg-N/L in 2006, which was the second-lowest total nitrogen value for any of the seven low-nitrogen plants (<3.0 mg-N/L) evaluated by EPA in 2006 (U.S. EPA 2008). About 1.9 pounds of methanol were added per pound of nitrate-nitrogen entering the denitrification system.

4.4.3 De Groote Lucht, Vlaardingen, Netherlands

In Vlaardingen, Netherlands, the 27.5-MGD De Groote Lucht WWTP was upgraded in 1999 to include biological denitrification (http://www.water.siemens.com). The plant consists of a two-stage aerobic treatment system for BOD removal and nitrification, followed by upflow continuous-backwash filters for denitrification.

Figure 4-11. De Groote Lucht WWTP. Source: Google Earth. Date of image: 12/07/2006

Methanol is added to the denitrification filters. An aeration system is used to strip nitrogen gas prior to chlorination and discharge. Because the plant is permitted to discharge an annual average of 10.0 mg/L-N, only about 75% of the plant flow is treated. From 2000 to 2002, the filters treated an average of 15.8 MGD, with an average influent nitrate level of 17.9 mg-N/L and an average effluent of 2.4 mg-N/L. About 3.3 pounds of methanol were added per pound of nitrate-nitrogen entering the denitrification system.

4.4.4 Seine-Centre, Paris, France

In Paris, France, the Seine-Centre WWTP treats an average dry-weather flow of 63.4 MGD. The plant has three separate biofiltration systems: the first for BOD removal the second for nitrification, and the last for denitrification, with methanol as the carbon source. The methanol addition is reduced by 30% in the summer when the effluent is used for agricultural irrigation. In 2005, the average influent nitrate concentration to the denitrification filters was 22.4 mg-N/L, with an effluent concentration of 2.3 for the year, excluding the summer, when it was about 15.

Figure 4-12. Seine-Centre WWTP. Source: Google Earth. Date of image: 10/20/2007

4.4.5 Jiashan City, China

In Jiashan City, China, a 5.3-MGD WWTP was designed and constructed in 2008 by Severn Trent Services. The plant has three separate biofiltration systems. Nitrified wastewater is recycled to the head end of the plant for mixing with influent. The first stage is an upflow anoxic filter for denitrification in which raw sewage is used as the carbon source. The second stage is an upflow aerated filter for BOD removal and nitrification. The third stage is a downflow filter for polishing denitrification and suspended solids removal. Methanol is added to the final stage as needed to meet the discharge standards. Pilot-plant studies showed a reduction in ammonia from 82 to 3 mg/L and total nitrogen from 88 to 11 mg/L, meeting China's Class 1A effluent standards.

Figure 4-13. WWTP in Jiashan City, China. Source: Google Earth. Date of image: 08/04/2010

5 Life-Cycle Analysis of Organic Carbon Sources

5.1 Introduction

The treatment of wastewater is an essential part of controlling the release of contaminants to the environment. Although directed primarily at the removal of bacteria and organic matter, as the world's population continues to grow, it is clear that nutrient management is an increasingly important issue. The presence of reactive nitrogen (Nr) has contributed to eutrophication and coastal hypoxia in over 400 estuaries worldwide, with few signs of improvement. Although much of the Nr that reaches these systems originates as agricultural and urban runoff, and atmospheric deposition, an important point source of Nr to these ecosystems is effluent from wastewater treatment plants. In order to meet mandated ammonia discharge requirements, most municipal systems in the United States practice nitrification, but only about 5% of Nr is removed through engineered denitrification treatment systems. Such tertiary nitrogen removal presents a method for removing a large portion of the nitrogen concentration from wastewater effluent before it is discharged. In an anoxic tertiary nitrogen removal system, an external carbon source is usually used to ensure that the denitrifying bacteria are not carbon limited.

This portion of the report examines alternative carbon sources for denitrification—methanol, ethanol, and acetic acid—using life-cycle assessment (LCA) methodology. LCA is a tool that allows for the impacts of a product or process to be compared across different life stages and impact categories. This ensures that the environmental burden is not being shifted from state to state, or location to location, in pursuit of environmental goals, and allows for the overall impact of the product to be examined.

5.2 Methodology

Sima Pro version 7.3.2 (Pre Consultants 2011) was used to carry out this analysis. It is a process-based software tool that facilitates the performance of LCA. Sima Pro uses several data libraries to generate the LCA information for a given product based on the sub-products and manufacturing processes that are needed to achieve the final end product. This includes not only the raw materials but also the energy needed for fabrication, transportation, use, and ultimately the end-of-life disposal of the product. This edition of Sima Pro includes several libraries. For this project, two different libraries were used: Ecoinvent from the Swiss Centre for Lifecycle Inventories (2012), and LCA Food DK from the Denmark Food Database (Nielsen et al. 2003).

LCA has the advantage of having a clearly defined and well-documented framework and methodology (SAIC 2006). The systematic approach of performing an LCA has four major parts: goals and scoping, inventory, impact, and assessment. The goal and scoping portion is critically important, because that is where the assumptions about the product or process are made, along with the scope of the project being defined. Scoping involves clearly defining the boundaries of the product or process to be studied, which typically has a large impact on the overall end result. In the inventory stage, the flows in and out of the system are identified and quantified. The flows typically include energy, water, and materials usage, along with environmental emissions. During the impact analysis, the impacts of the system are identified and assigned to impact categories, such as eutrophication and global warming. The assessment step is where the impacts are identified and interpreted. This step is where the product or process can be compared with others to determine the best option environmentally.

In modeling the impacts (sometimes referred to as life-cycle impact analysis, or LCIA), an appropriate impact assessment tool must be used. Several are available in the Sima Pro software. The tool used in this case is TRACI (Tool for the Reduction and Assessment of Chemical and other environmental Impacts) which was developed by the U.S. EPA (2012). TRACI was created to be applied to the impact assessments of sustainability metrics, LCA, industrial ecology, process design, and pollution prevention. Unlike other impact assessment tools, TRACI was developed specifically for the United States and uses an approach consistent with input parameters and locations in the United States. TRACI allows for the following impact categories: ozone depletion, global warming, acidification, eutrophication, tropospheric ozone formation (smog), ecotoxicity, human particulate effects, human carcinogenic effects, human non-carcinogenic effects, fossil-fuel depletion, and land-use effects (Bare 2002). In this study nine impact categories were used; Table 5-1 presents these impact categories and the basis for units of expression.

Table 5-1. Impact categories

Impact Category	Unit Explanation (Units per kg nitrate removed)
Global Warming	The units here are kg of CO_2e (carbon dioxide equivalents). Carbon dioxide equivalents are a method of accounting for different greenhouse gases and normalizing them to a single unit.
Acidification	The units of acidification impact are H+ moles eq. This unit is in terms of the equivalent mass of the acid which can supply one mole of H+.
Carcinogenics	The unit is kg of benzene equivalents (a carcinogen). This unit represents the number of kg of benzene that would have to be emitted to pose the same health risks as the individual carcinogenic impacts.
Non-Carcinogenics	The units in this case are expressed in terms of kg toluene equivalents. Toluene, a non-carcinogen, is used to normalize the effects of the various chemicals to the equivalent mass of toluene needed to produce the same level of impact.
Respiratory Effects	The units for this measurement are in kg of $PM_{2.5}$ eq, which is particulate matter with a diameter of 2.5 µm (microns) or less. Particles of this diameter and smaller have been linked to respiratory issues. This allows the respiratory impacts to be normalized on a basis of impact equivalent to $PM_{2.5}$.
Eutrophication	Nitrate has a large eutrophication impact, and due to its avoidances, the eutrophication impact values are negative. Thus, the smaller of the negative values has the larger impact. The units utilized here are kg nitrogen eq, which is a unit based on eutrophication impact, which allows for normalization to the equivalent impact that a kg of nitrogen would have.
Ozone Depletion	Units for this impact are kg CFC-11 (trichlorofluoromethane). CFC-11 is a compound that degrades the ozone layer. This unit term is utilized to normalize the ozone depletion impacts to the equivalent mass of CFC-11.
Ecotoxicity	This impact is measured in units of 2,4-D eq (dicholorophenoxyacetic acid), a pesticide and herbicide. The equivalency measure allows the ecotoxicity impacts of the different ethanol product processes to be normalized into one unit of impact equivalent to 2,4-D.
Smog	The units used to express this are g NOx eq, which is grams of NO (nitrogen oxide) and NO_2 (nitrogen dioxide), which are nitrogen compounds generated during fossil fuel combustion that cause photochemical smog. This unit is utilized to normalize the impacts of the emissions to an equivalent impact from a mass of NOx.

5.3 System Boundaries

As with any LCA, it is important to clearly define the scope and boundaries of the project. The overarching goal of this project was to examine the impacts of different external carbon sources for tertiary denitrification in a wastewater treatment system. In this case, the boundaries include the fabrication of the external carbon sources, the transportation of the external carbon sources to the WWTP, and the operation of the denitrification filter (Figure 5-1).

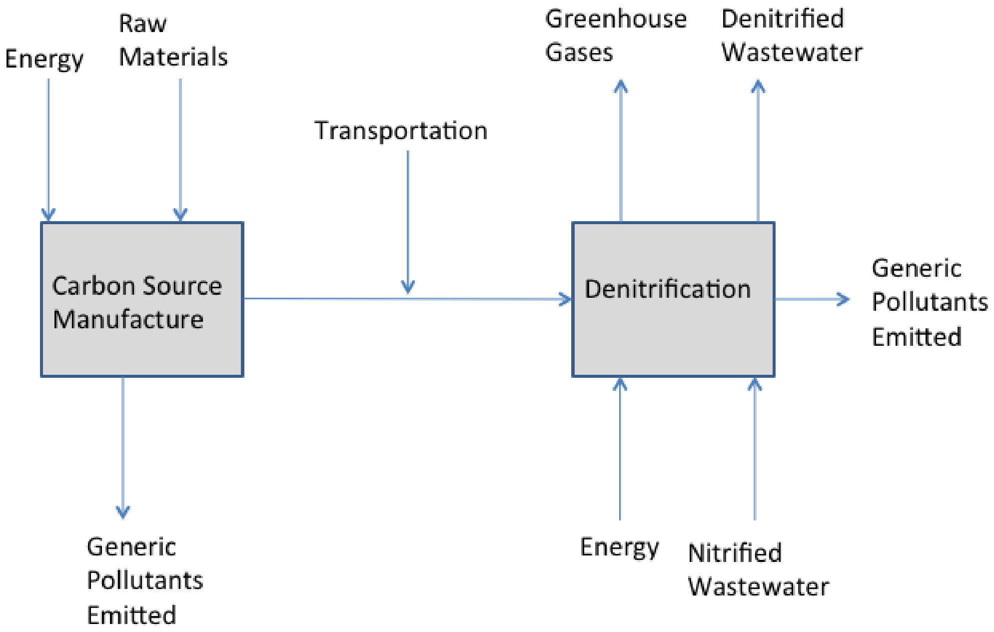


Figure 5-1. System boundaries

5.4 Assumptions

It was assumed that the following three stoichiometries are valid (Metcalf and Eddy 2003).

$$5CH_3OH + 6NO_3^- \rightarrow 5CO_2 + 7H_2O + 6OH^- \quad (1)$$

$$5CH_3CH_2OH + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 15H_2O \quad (2)$$

$$5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 8OH^- \quad (3)$$

Several additional assumptions were made for this LCA. The first assumption was that a 50% stoichiometric excess of the three external carbon sources—CH_3OH (methanol), CH_3CH_2OH (ethanol), and CH_3COOH (acetic acid)—would be used for the analysis. The second was that the function unit of the analysis would be impact per kilogram of NO_3- (nitrate) removed.

To account for transportation of the different carbon sources, general start and end points had to be determined. For all transportation trips, it was assumed that the majority of the trip was completed via rail, with the remaining 100 miles completed via truck. This assumption accounted for the general distance of taking the external carbon source from the rail depot to the treatment plant. The distance for each carbon source was computed to Chesapeake Bay, an area with a well-known excess nutrient problem. It was also assumed that all of the carbon sources were being manufactured in the United States. The majority of U.S. methanol production occurs in the Houston area (Jordan and Maloy 2002). The computed distance from Houston to the Chesapeake Bay was found to be 1485.9 miles; of this, 1385.9 miles were allocated to rail, and 100 miles were allocated to truck transportation. Ethanol is produced primarily in the Midwest, and the center point was taken to be Sioux City, Iowa (Renewable Fuels Association 2012); thus, the distance for ethanol transportation was 1255 miles, with 1155 miles allocated to rail and 100 miles allocated to truck. The data on acetic acid manufacture in the United States are limited, but the largest U.S. producer of acetic acid is BP (British Petroleum), whose main plant is in Texas City, Texas (British Petroleum 2012). This is 1490 miles distant from the Chesapeake, so 1390 miles were allocated to rail and 100 miles to truck.

It was assumed that an anoxic down-flow filter would be used for tertiary wastewater treatment (Figure 5-2).

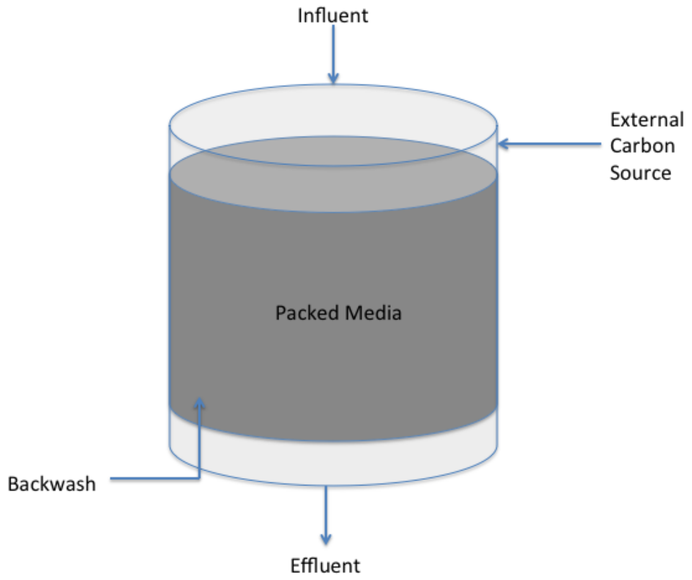


Figure 5-2. Down-flow anoxic filter

Due to the relatively long life span of the anoxic filter itself (taken to be approximately 30 years), it was assumed that the construction and disposal impacts of the filter materials could be neglected. It was also assumed that wastewater would enter the filter already fully nitrified from the activated sludge system. The energy demand of the filter includes pumping and backwashing; it was assumed that the backwashing was performed using wastewater, and therefore, cleaning of the backwash water did not need to be incorporated. The energy demand of the filter was found to be 0.197 kwhr (kilowatt-hour) to remove 1 kg of NO_3^- (Wang et al., 2009). This was calculated using a filter capacity of 10 MGD, or 37.85 million liters per day. The influent NO_3^- concentration of the filter was assumed to be 25 mg NO_3-N/liter, and the effluent was assumed to be 2 mg NO_3-N/liter.

It was assumed that coal was the energy source used to generate electricity for the operation of the denitrification filter. The chemical emissions from denitrification were based on the above stoichiometry. It was assumed that all of the nitrogen removed was released as N_2 (nitrogen gas) and that all of the carbon became CO_2 (carbon dioxide) (Table 5-2). This assumption—that all of the nitrogen removed becomes N_2—is the conventional thought in wastewater engineering; however, recent research has shown that this may not be an entirely valid assumption, and that intermediates to the process such as N_2O would also be emitted (Ahn et al. 2010).

Table 5-2. Greenhouse gas emissions by carbon source

External Carbon Source	N2/kg NO3- removed	CO2/kg NO3- removed
Methanol	0.225	0.591
Ethanol	0.225	0.791
Acetic acid	0.241	0.950

5.5 Results

The relative impact in each of the impact categories explored is also mapped in Appendix A. This allows for the products and processes with the most impact to be viewed. Depending on which impact category is being viewed, different processes may have a larger impact on the same carbon source.

Ethanol can be produced from several different sources, including corn, sorghum, switchgrass, and ethylene (the latter a fossil source). In the United States, ethanol is produced predominantly from corn, a biomass source. It is important to note that the impacts of ethanol for denitrification can vary based on the method by which the ethanol is produced (Table 5-3). Charts displaying the differences between the two different types of ethanol are located in Appendix B. In this analysis, the impacts of both sources of ethanol were computed. The negative values in the "eutrophication" category are due to the functional unit being used here: kg NO_3^- discharge to water avoided.

Ethanol from fossil sources has a lower impact in seven of the nine impact categories explored, while ethanol from corn has a lower impact in the remaining two categories. This means that, absent any sort of weighting scheme, ethanol from fossil sources may have an overall lower impact than ethanol from corn. However, if the decision is based on just one or two categories that are deemed critically important for a given area (say, smog formation in an urban region), then it is possible than ethanol manufactured from corn could be considered the better source.

Table 5-3. Impacts of ethanol for denitrification

Impact Category	Ethanol-Fossil	Ethanol-Corn	Units/kg NO_3^- removed
Global Warming	1.7	2.07	kg CO_2e
Acidification	0.207	0.487	H+ moles eq
Carcinogenics	0.00166	0.00381	kg Benzene eq
Non-Carcinogenics	11.8	18.4	kg Toluene eq
Respiratory Effects	0.000956	0.00129	kg PM 2.5 eq
Eutrophication	-0.234	-0.22	kg N eq
Ozone Depletion	$7.28*10^8$	$1.46*10^7$	kg CFC-11 eq
Ecotoxicity	1.36	1.29	kg 2,4-D eq
Smog	0.00348	0.00337	g NO_x eq

Ethanol from corn was compared with methanol and acetic acid for NO3- removal in a tertiary denitrification filter for wastewater treatment (Figure 5-3, Table 5-4).

The results overall favor methanol; however, in LCA, it is important to examine all impact categories when comparing results. Depending on which impact category is most important, it is straightforward to see impacts of different carbon sources on denitrification. Charts displaying the differences among the impacts of the three different types of carbon sources are presented in Appendix B. The colors used in Table 5-3 illustrate the external carbon source with the lowest impacts (green) and the highest impacts (red) of the carbon sources studied.

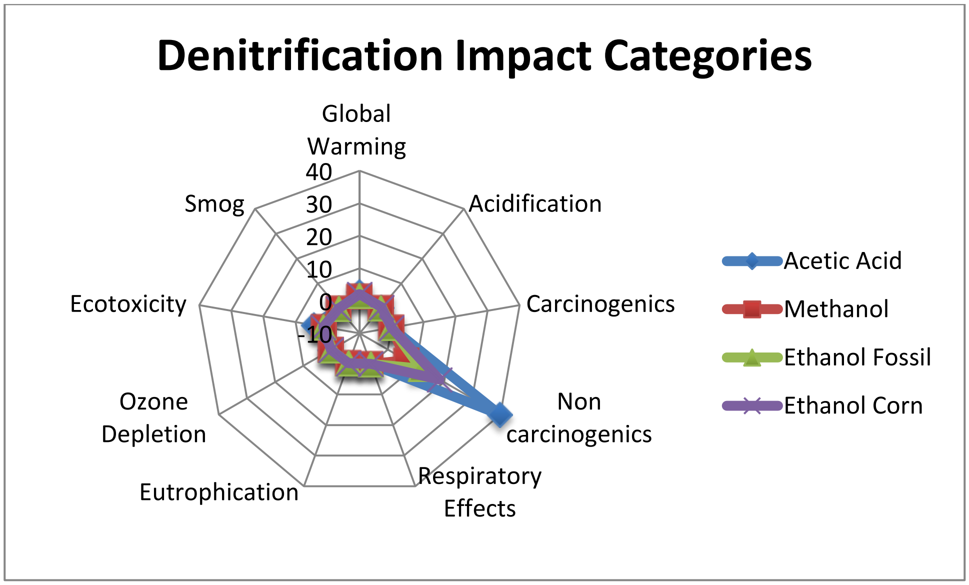


Figure 5-3. Spider plot of denitrification impact categories by carbon source

Table 5-4. Impacts of three carbon sources for denitrification

Impact Category	Methanol	Ethanol (from corn)	Acetic Acid	Units/kg NO3- removed
Global Warming	1.4	2.07	2.71	kg CO2e
Acidification	0.152	0.487	0.408	H+ moles eq
Carcinogenics	0.00108	0.00381	0.00585	kg benzene eq
Non-carcinogenics	6.63	18.4	39.8	kg toluene eq
Respiratory Effects	0.000683	0.00129	0.00213	kg PM2.5 eq
Eutrophication	-0.235	-0.220	-0.229	kg N eq
Ozone Depletion	0.165	0.146	0.339	kg CFC-11 eq
Ecotoxicity	1.12	1.29	4.32	kg 2,4-D eq
Smog	0.00176	0.00337	0.00488	g NOx eq

In the nine impact categories presented, methanol has the lowest impact of the three carbon sources compared in eight of the categories. The exception to this is ozone depletion, where ethanol has the lowest impact. Acetic acid has the greatest impacts in seven of the categories, with the exception of acidification and eutrophication, where ethanol has the highest impact. It is logical that acetic acid would have a greater impact than methanol due to the fact that it is fabricated from methanol. Ethanol has the lowest impact in the ozone depletion category, the highest impact in the acidification and eutrophication categories, and an impact between the two extremes in the other seven categories. Again, if certain impact categories were deemed extremely significant in a sensitive area, that impact category would be weighed more heavily when comparing the options to select the best choice of carbon sources.

5.6 Conclusions

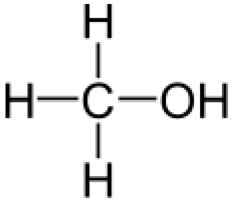
Tertiary denitrification presents an opportunity to remove NO_3^- from wastewater before discharging it back to the environment, with resulting reduced impact from eutrophication due to excess nitrogen in the aquatic environment. Coastal estuaries often are particularly sensitive to nitrogen loading. All three of the external carbon sources examined for tertiary nitrogen removal are capable of removing nitrogen from wastewater; however, in terms of environmental impact, they are not all the same.

In terms of relative environmental impact among the three external carbon sources, methanol has the lower impact in most categories, with acetic acid having the greatest impacts. However, in determining which among the external carbon sources examined is the most environmentally friendly, a weighting schema of the impacts would need to be applied based on those impact categories deemed the most important.

6 Methanol Properties, Safety and Health

6.1 Physical Properties

Methanol is the simplest aliphatic alcohol containing a single carbon atom, three hydrogen atoms (the CH_3 methyl group), and an attached hydroxyl group (OH), as shown below:



Methanol's chemical abstract service registry number is 67-56-1.[2] It is a volatile, colorless liquid that is lighter than water (specific gravity is approximately 0.8).[3] Its boiling point is 65.4°C (149°F), and its freezing point is –98°C (–144°F). It is miscible (100% soluble) in water and can be used as an anti-freeze; for example, a solution of 25% methanol by weight will freeze at approximately –20°C (–4°F).

Methanol vapors are heavier than air (specific density is 1.11) and flammable. Methanol vapor will burn in the presence of an ignition source at concentrations between 6% by volume (the lower explosive limit, or LEL) and 36% (the upper explosive limit, or UEL); outside of this range, the vapors are either too dilute (lean) or too concentrated (rich) to combust. The flash point of pure methanol is approximately 12°C (54°F).[4] Methanol vapors have a light, sweet odor and can typically be detected at concentrations in the range of 100 ppm to 2,000 ppm (0.01% to 0.2% by volume).[3]

6.2 Storage, Handling, and Use

Methanol is defined by the U.S. National Fire Protection Association (NFPA) and Occupational Safety and Health Administration (OSHA) as a Class 1B flammable liquid, or by the United Nations as a flammable liquid (UN Hazard Class 3). It is also toxic to humans and the environment if exposure and releases occur. Safe storage, handling, and use of methanol are therefore important concerns.

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[2] Synonyms include carbinol; methyl hydroxide; methylol; monohydroxymethane; wood alcohol;colonial spirit; columbian spirit; hydroxymethane; wood naphtha; alcool methylique; alcool metilico; columbian spirits; metanolo; methylalkohol; metylowy alkohol; pyroxylic spirit;wood spirit;pyro alcohol;spirit of wood.

[3] Source: Hazardous Substances Databank (HSDB) http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~d456bf:1

[4] Flash point is defined as the minimum temperature at which the vapor pressure of a liquid is sufficient to form an ignitable mixture with air near the surface of the liquid.

The Methanol Institute has developed guidance for methanol users that addresses a number of key issues related to the safe handling, storage, and use of methanol at a site. The *Methanol Safe Handling Manual* (SHM) provides background information on its uses, physical and chemical properties, health and safety, process safety, fire safety, storage, emergency response, and other items (MI 2012).[5] NFPA Code #30, *Flammable and Combustible Liquids Code*, provides "fundamental safeguards for the storage, handling, and use of flammable and combustible liquids," including methanol (NFPA 2012). OSHA standard 1910.106, *Flammable and Combustible Liquids*, also applies to methanol installations. It is recommended that the reader become familiar with the contents of the *Methanol Safe Handling Manual*, NFPA 30, OSHA 1910.10, and all relevant guidance and national and local regulations that may apply to the use, handling, and storage of methanol.

The guidance summarizes key aspects of storage, handling, and use of methanol, based mainly on the above NFPA (2012) and the MI's SHM. It is not, however, intended to be comprehensive or in any way to replace guidance and regulations.[6]

Number	Degree of Hazard
4	Extreme
3	Serious
2	Moderate
1	Slight
0	Minimal

Figure 6-1. NFPA chemical hazard labels, with methanol label on the right

6.3 Storage

Although there are many means of storing methanol (e.g., totes, drums, tanks), it is anticipated that, at wastewater treatment facilities, it will most likely be stored in outdoor, aboveground fixed tanks at atmospheric pressure, with aboveground piping. Storage tanks should be steel or an approved noncombustible material. Methanol storage containers should be made of materials that it will not corrode. Tanks should meet with all applicable and appropriate design standards; for example, ANSI/UL 142, *Standard for Steel Aboveground Tanks for Flammable and Combustible Liquids*, and UL 2080, *Standard for Fire-Resistant Tanks for Flammable and Combustible Liquids*. A number of requirements covering aspects such as venting, corrosion protection, linings, thermal insulation, and testing, including tightness testing, will need to be met. It is recommended that tanks be painted with heat-reflecting paint to reduce formation and loss of vapors.

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[5] http://www.methanol.org/Health-And-Safety/Safe-Handling/Methanol-Safe-Hanlding-Manual.aspx

[6] Portions of the SHM have been incorporated into this document, with the MI's approval.

Figure 6-2. Large methanol storage tanks with secondary containment

Figure 6-3. Steel tank with concrete secondary containment[7]

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[7] Source of image: Severn Trent Services

Figure 6-4. Double contained concrete tank with steel inner tank (no additional containment required)[8]

All storage devices, including totes and drums, require secondary containment (e.g., berming) and adequate ventilation. Berming should be stabilized by compacting, by use of suitable methanol-resistant fabric, or with concrete. The solvent properties of methanol are such that hydrocarbon residuum, asphalt, and road oil are not suitable as berm cover or stabilization materials.

Methanol should be stored and used in a dedicated area that is specifically marked and appropriately labeled. This area should have safety measures readily available to employees working in the area. The area designated for methanol handling should be equipped with an effective audible alarm that will summon assistance in a timely manner. The area should be designated as a hazardous area, and protective measures should be immediately available in the event of a spill, exposure, or ignition. Methanol must not be stored near oxidizing compounds such as, but not limited to, bromine, sodium hypochlorite, and chlorine.

6.4 Fire Prevention and Control

Fire control methods are critical to methanol storage facilities. Effective measures will minimize the potential for human injury and property damage in the event of a fire. Vapor control and control of ignition sources are essential components of fire control.

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[8] Source of image: Severn Trent Services

Methanol burns with a clear blue flame that can be difficult to see in bright light or sunlight, and the only indication may be a shimmering "heat haze." It is possible, though highly unlikely, that spectators or firefighters might fail to notice the heat and unknowingly walk into a methanol fire. In the great majority of fires, however, burning materials (such as building materials, engine oil, upholstery, paint, etc.) would produce both smoke and visible flames. Methanol fires produce less heat (have a low flame temperature) than other fuels, transfer less heat to surroundings (flames are non-luminous), can initiate under unexpected circumstances (flammability limits are between 6 vol% and 36 vol% in air), are difficult to extinguish with water (100% miscible), and are flammable to 75 vol% water.

Two instrumentation technologies are available for early detection of a methanol fire. The first is vapor detection. If a methanol source is emitting large quantities of vapor, it is only a matter of time before ignition and flashback occur. Early detection increases the chance that the source of vapor can be isolated and mitigated before the vapors ignite. The second technology is thermal imaging. This has been used for many years to identify hot spots and loose connections in electrical systems. It works equally well on methanol fires.

Methanol has a low flash point of 54°F, which is often exceeded by ambient temperatures. Contained or uncontained methanol vapors are therefore readily ignitable. Vapor formation within tanks can best be minimized by use of internal floating roofs or inert blanketing gases such as dry nitrogen. Nitrogen padding has the added advantage of preserving methanol purity. Dry nitrogen is the preferred gas for blanketing. Blanket gas should be free of carbon dioxide, to avoid corrosion in the presence of moist air, and to avoid product contamination that could increase methanol acidity and corrosivity. Inert gas blanketing or padding adds an additional level of protection against ignition within the tank vapor space. Because nitrogen gas is an asphyxiant, special precautions should be taken for accessing the tank roof, and for entering purged tanks.

If the vapor space of the tank is not padded with an inert gas, then the tank vents should be equipped with flame arresters. Tank internal pressure can be controlled using pressure relief/vacuum breaker valves. Vents may or may not be configured with flame arresters, depending on the specific circumstances; however, arresters are the preferred configuration. The flame arrester components should not be fabricated of aluminum alloy, because methanol is corrosive to aluminum alloys.

Pressure relief valves are sized to a fire case and, if possible, should be piped to relieve into a flare header. If configured to relieve to the atmosphere, then it is strongly recommended that process safety valves (PSVs), be configured to breathe to the atmosphere through flame arresters. In addition to fire safety, it is recommended that local regulations for limiting hydrocarbon emissions be considered when configuring tank vents and pressure relief devices. Overflow pipes are not recommended. Methanol liquid is known to collect and drip from overflow pipes when the ambient temperature is below the storage temperature. Any accumulation of condensed liquid methanol in the bermed area may create a fire hazard and may qualify as an environmental release.

Figure 6-5. Pressure/vacuum relief valve and flame arrestor (red box)[9]

Ignition sources should be strictly controlled within the proximity of methanol storage, regardless of whether containment is in tanks or portable containers. NFPA (2012) lists the following as examples of ignition sources: open flames, lightning, hot surfaces, radiant heat, smoking, spontaneous ignition, cutting and welding, frictional heat and sparks, static electricity, electrical sparks, stray current, ovens, furnaces, and heating equipment. Smoking must be restricted to a designated location that is free of potential methanol vapor. Vehicle access must be strictly controlled and enforced. Use of non-sparking tools is highly recommended. Radios, telephones, portable instrumentation, computers, calculators, and other electronic equipment should have a fire-safe, explosion-proof rating to be used in a methanol containment area.

Electrical equipment within the proximity of methanol storage and handling must be explosion-proof to meet electrical code requirements (e.g., National Electrical Code). Positive pressure may be required to ensure that methanol-free areas, such as smoking rooms and control systems and electrical switch gear, are protected.

Grounding is especially important in protecting methanol from accidental ignition resulting from static discharge. Tanks must be grounded to avoid hazards associated with static discharge. Grounding is required for lighting systems, pipe racks, pumps, vessel, filters, and all other equipment near and potentially within range of methanol vapor. Tall towers and other equipment subject to lightning strike must be equipped with lightning arresters.

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[9] Source of image: Severn Trent Services

6.5 Piping, Handling, and Transfer Systems

Performance standards for piping systems for flammable liquids in the U.S. include NFPA (2012), OSHA 1910.106, and the American Society of Mechanical Engineers (ASME) B31 Code for Pressure Piping. Materials for aboveground piping, valves, or fittings shall be steel or ductile (nodular) iron of appropriate specification or other materials that are appropriate for the conveyance of methanol and meet with applicable codes. Leak detection and alarm is recommended.

The use of PVC piping, valves, or fittings etc., is strongly discouraged, because this type of piping is less able to withstand forces that may be exerted on the system in the event of a tank explosion or similar event—the use of PVC piping contributed significantly to the severity of an incident involving a tank explosion in the U.S.[10]

Figure 6-6. Methanol storage transfer station

Precautions for methanol transfer are much like those for gasoline. Methanol transfer operations should be bonded and grounded. Containers should also be grounded and bonded when transferring material, in order to avoid static sparks. Hoses must be grounded. In methanol loading and unloading situations, the possibility of spark generation due to accumulation of static electricity is less than with materials such as low-sulfur diesel. Methanol is not a static accumulator. Nevertheless, velocity limits should be placed on transfer operations that involve high pressure drop, hydraulic impacts, and erosion concerns. Refer to API and NFPA publications for specific guidance.

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[10] U.S. Chemical Safety and Hazard Investigation Board. Investigation Report. Report No. 2006-03-I-Fl. March 2007. Methanol Tank Explosion and Fire. http://www.csb.gov/assets/document/Bethune_Final_Report.pdf

Figure 6-7. Methanol delivery by tanker truck

Metal containers (drums or totes) and the associated fill equipment pump should be bonded together and grounded during methanol transfer operations. Fill pipes or hoses should be conductive and should be bonded to the filling system.

6.6 Health

In addition to being a potential fire hazard, methanol can be toxic to humans and the environment. Methanol can cause health effects if ingested, inhaled, or contacted by skin. Therefore, it is important to avoid breathing vapor, mist, or gas and minimize the potential for getting methanol in the eyes and on skin or clothing.

6.7 Exposure

It should be recognized that humans are exposed to methanol from many sources. Not only does methanol occur naturally in the human body, but humans are exposed routinely to methanol through air, water, and food. Food is the primary source of exposure for the general population. It is generally believed that dietary sources contribute to the observed background blood methanol concentrations. Methanol is widely found in small concentrations in the human diet from fresh fruits; vegetables; and commercial beverages such as fruit juices, beers, wines, and distilled spirits.

Occupational (workplace) exposure is likely to cause the highest daily exposure to methanol. Occupational exposures typically occur through inhalation of methanol vapors during production or use. The Occupational Safety and Health Administration (OSHA) time-weighted-average (TWA) permissible exposure limit (PEL) to methanol is 200 ppm for an 8-hour day and 40-hour week.

Methanol's primary routes of entry into the body are by inhalation, absorption through the skin as a result of contact, eye contact, and ingestion by either eating or drinking. Methanol is easily and rapidly absorbed by all routes of exposure and distributes rapidly throughout the body. Humans absorb 60%–85% of the methanol that is inhaled. A small amount is excreted by the lungs and kidneys without being metabolized. The rate of metabolism for methanol in the body is 25 mg/kg-hr, which is seven times slower than for ethanol and is independent of concentrations in the blood. Humans metabolize methanol into formaldehyde as the first step. The formaldehyde is then converted to formate, which can be toxic at high concentrations, and finally, to carbon dioxide and water. The half-life of methanol elimination in expired air after oral or dermal exposure is 1.5 hours. Due to their limited capability to metabolize formate to carbon dioxide, humans accumulate formate in their bodies from high-dose methanol exposure. If formate generation continues at a rate that exceeds its rate of metabolism, methanol toxicity sets in. Background levels of methanol in the human body will not result in formate accumulation or adverse health effects. Studies have shown that short-term inhalation exposure to 200 ppm methanol results in blood methanol concentrations of less than 10 mg/L, with no observed increase in blood formate concentration.

Methanol is a poison. This means that it can cause severe and sometimes fatal acute toxic effects from a single exposure. At this time, there is no known method of mitigating its toxic effects. Therefore, the principal concern is with acute exposure through any primary routes of entry. The signs and symptoms of methanol exposure do not occur immediately. The time lag between exposure and onset of symptoms may cause misdiagnosis of the cause, particularly in persons who are unaware that they have been exposed, or who are unaware of the toxic nature of methanol and the differences between methanol, ethanol, and isopropyl alcohol.

6.8 General Symptoms

The toxicity of methanol is the same, regardless of the route of exposure. Signs of systemic toxic effects may be delayed between 8 and 36 hours after initial exposure. Methanol is irritating to the eyes, the skin, and the respiratory tract. It also strips the natural oils and fat from the skin, causing skin to become dry and cracked. It can cause permanent damage to the optic nerve and central and peripheral nervous system with just a single acute exposure. Other signs and symptoms of methanol poisoning include headache, dizziness, vomiting, severe abdominal pain, back pain, difficulty breathing, cold extremities, lethargy, and lack of coordination. Eye exposure can also cause a burning sensation accompanied by tearing, redness, and swelling. Direct contact with the liquid may cause conjunctivitis and corneal burns. High exposures may result in blindness and death.

6.9 Acute Effects

The effects of acute, high-dose methanol exposure have been well characterized in human cases of alcohol poisoning and in animal studies. Generally, the affected individual experiences a short period of intoxication with a mild depression of the central nervous system, followed by a period in which no symptoms of intoxication or toxicity are noted (commonly 12 to 14 hours). This is followed by physical symptoms of poisoning, such as headache, nausea, vomiting, loss of equilibrium, severe abdominal pain, and difficulty in breathing. These symptoms can be followed by coma and death. Other hallmarks of acute methanol toxicity are disturbances of the visual system and accumulation of acid in the body. Methanol exposure results in vision effects that range from excessive sensitivity to light, misty or blurred vision, to dramatically reduced visual acuity and total blindness.

6.10 Chronic Effects

In contrast to the effects of acute, high-concentration exposure, relatively little is known about the effects of chronic, low-dose methanol exposure. Based on the limited number of case reports and epidemiologic studies, the effects of prolonged exposures to methanol are similar to those of acute exposure: visual and central nervous system disorders. Repeated direct skin contact with methanol can cause dermatitis with dryness and cracking. Other symptoms of chronic exposure include eye irritation, headache, giddiness, insomnia, gastrointestinal problems, and especially visual difficulties.

According to the Organization for Economic Cooperation and Development's (OECD's) Screening Information Data Set, methanol is a candidate for further work on human health effects due to potential hazardous properties, including neurological effects, central nervous system (CNS) depression, ocular effects, reproductive and developmental effects, and other organ toxicity.

Methanol is not currently listed as being a carcinogen by any international consensus body or government agency (e.g., IARC, NTP, NIOSH, ACGIH, or OSHA). EPA's Integrated Risk Information System (IRIS) is conducting a human health hazard and dose-response assessment of methanol. A draft IRIS Toxicological Review of Methanol released for external peer review in December 2009 concluded that the weight of evidence is consistent with a determination that methanol is likely to be carcinogenic to humans. This is defined as "an agent that has tested positive in animal experiments in more than one species, sex, strain, site, or exposure route, with or without evidence of carcinogenicity in humans." The Methanol Institute submitted written comments to EPA in a report entitled "Methanol Institute's Comments on the Draft Toxicological Review of Methanol (IRIS)," on March 15, 2010. The Methanol Institute believes that the underlying science demonstrates instead that methanol merits a classification of "Inadequate Information to Assess Carcinogenic Potential" under EPA's 2005 Guidelines for Carcinogen Risk Assessment. In March 2011, EPA placed the external peer review of the draft IRIS Methanol Toxicological Review on hold, following a report from the National Toxicology Program (NTP), which recommended a review to resolve differences of opinion in the diagnoses of certain tumors reported in a methanol research study completed by a European research institute. In March 2012, EPA announced that it has decided not to rely on data from the European research institute in the IRIS assessment for methanol. According to the draft IRIS Toxicological Review, "There is no information available in the literature regarding the observation of cancer in humans following chronic administration of methanol."

Likewise, there are no human data that demonstrate a link between methanol exposure and an increased incidence of birth defects or reproductive hazards. However, available data on mice and rats indicate that inhalation or oral exposure to methanol at high doses is a developmental hazard. Mice and rats metabolize methanol differently from humans, so there is uncertainty as to the predictive value of these studies to human health effects. There is concern for adverse developmental effects in fetuses if pregnant women are exposed to methanol at levels that result in high blood methanol concentrations greater than 10 mg/L. Blood methanol levels of 10 mg/L or greater are not expected to result from normal dietary sources or from occupational inhalation exposures at air concentrations below the methanol PEL. However, this value is not intended to represent the highest “safe” blood concentration.

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Appendix A: LCA Process Flow Diagrams

Process flow diagrams in regards to LCA allow for the contributing processes and products to be shown visually in regards to their contribution to the impact. The thickness of the line is proportional to the relative quantity of the impact that the product or process is contributing to the overall denitrification impact. In the diagrams below not all links and nodes in the network are visible, only the links and nodes that make large contributions in the impact in that category, however, all links and nodes are taken into account in generating the impacts. In utilizing acetic acid for denitrification, the largest global warming impact is due to the generation of acetic acid (Figure A-1).

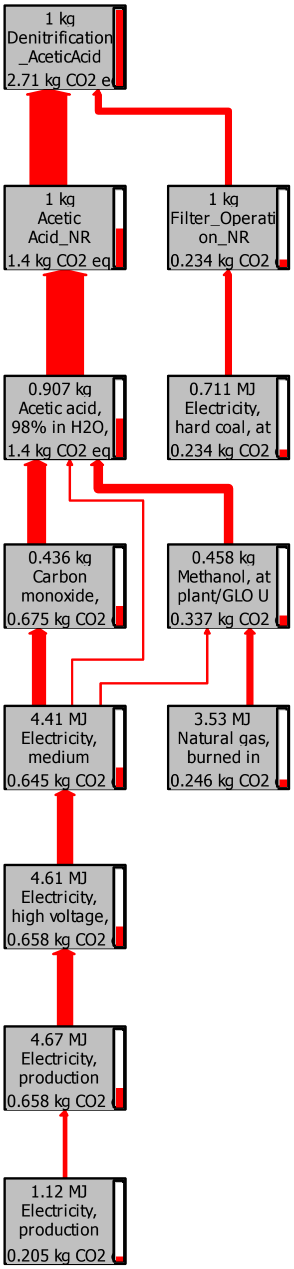

Figure A-1. Process flow diagram of acetic acid for global warming impacts

In utilizing acetic acid for denitrification, the greatest impact in terms of acidification is due to acetic acid production with contributions from filter operation and transportation (Figure A-2).

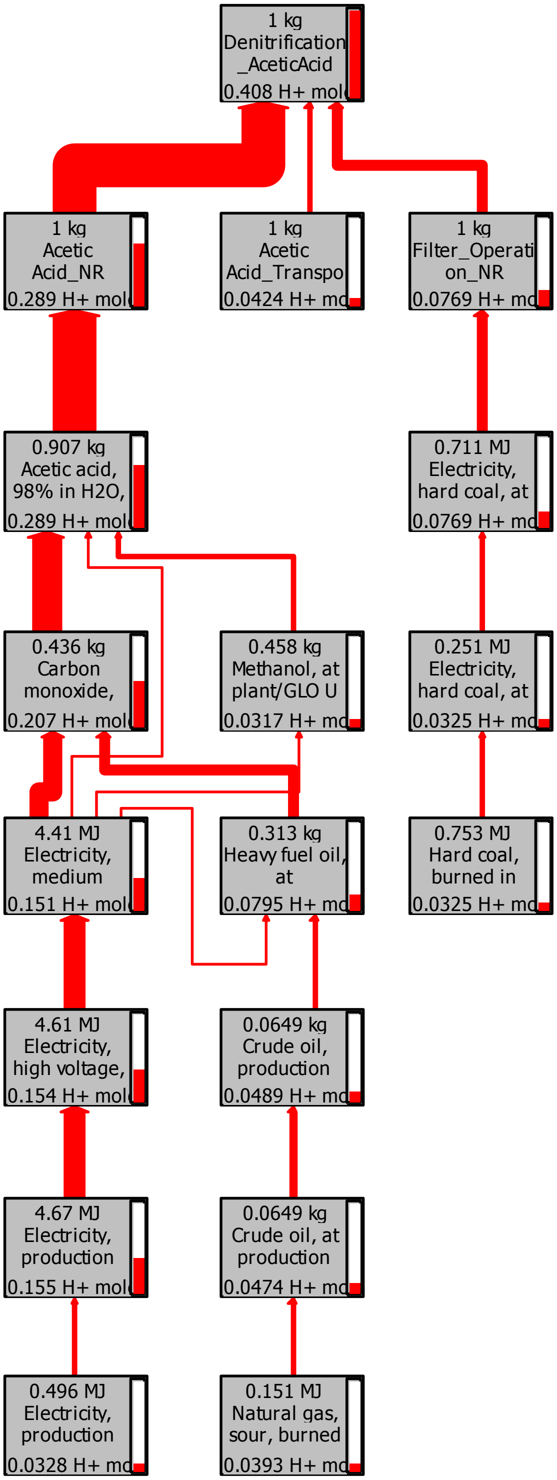

Figure A-2. Process flow diagram of acetic acid impacts for acidification impacts

In utilizing acetic acid for denitrification, the greatest impact in terms of carcinogens is due to acetic acid production (Figure A-3).

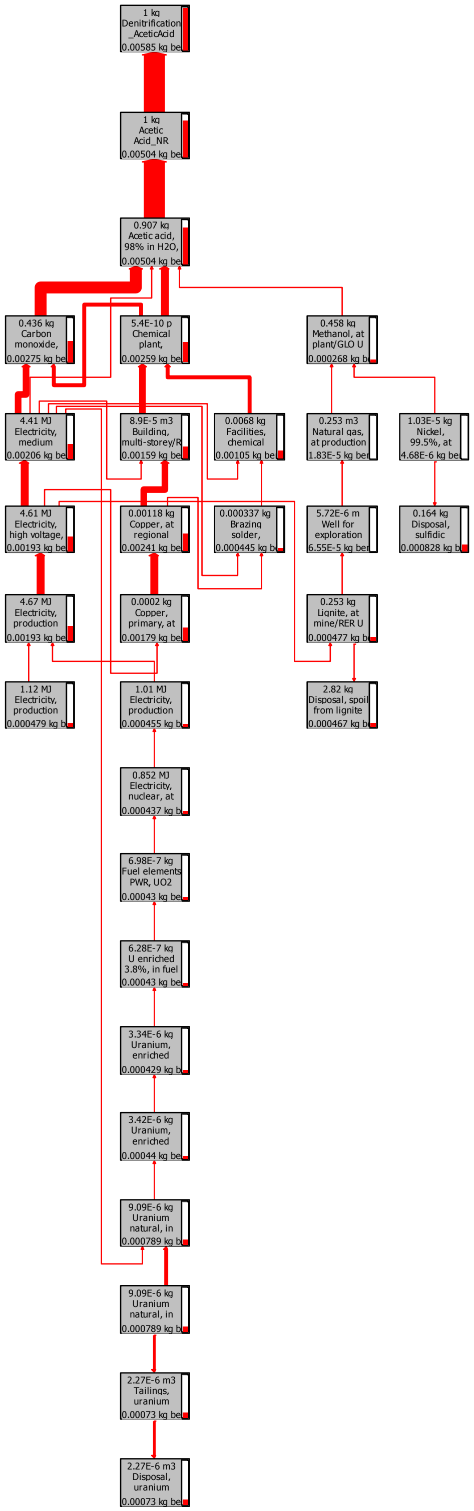

Figure A-3. Process flow diagram of acetic acid for carcinogen impacts

In utilizing acetic acid for denitrification, the greatest impact in terms of non-carcinogen air pollutants is due to acetic acid production (Figure A-4).

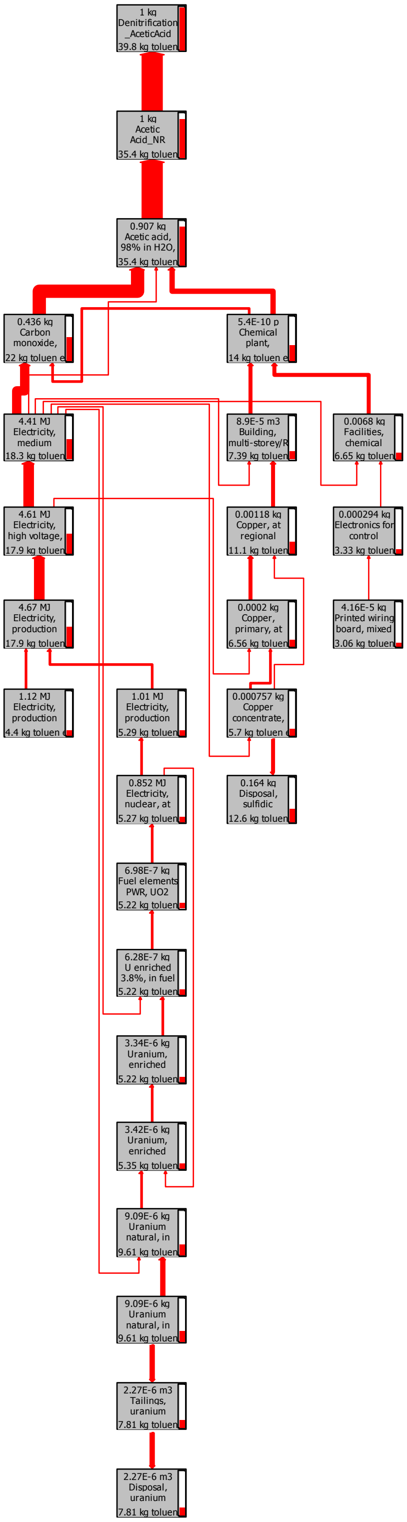

Figure A-4. Process flow diagrams of acetic acid for non-carcinogenic air pollutant impacts

In utilizing acetic acid for denitrification, the greatest impact in terms of respiratory effects is due to acetic acid production, followed by the operation of the filter (Figure A-5).

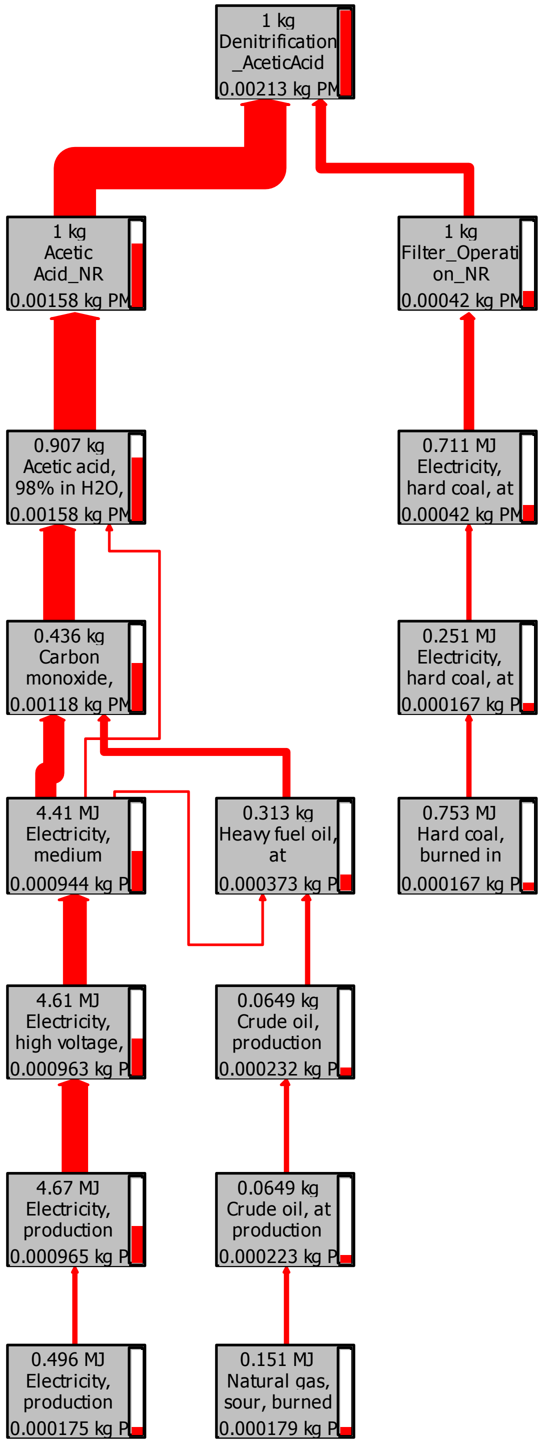

Figure A-5. Process flow diagram of acetic acid for respiratory health impacts

In utilizing acetic acid for denitrification, the impact in terms of eutrophication is negative, hence the green arrow (Figure A-6). This is due to the fact that there are no large eutrophication impacts due to the use of acetic acid for denitrification, which means that this is a negative impact.

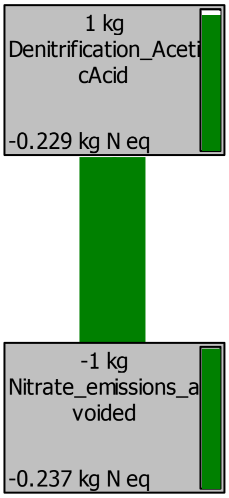

Figure A-6. Process flow diagram of acetic acid for eutrophication impacts

In utilizing acetic acid for denitrification, the impact in terms of ozone depletion is due mainly to acetic acid production with a small portion of the impact from transportation (Figure A-7).

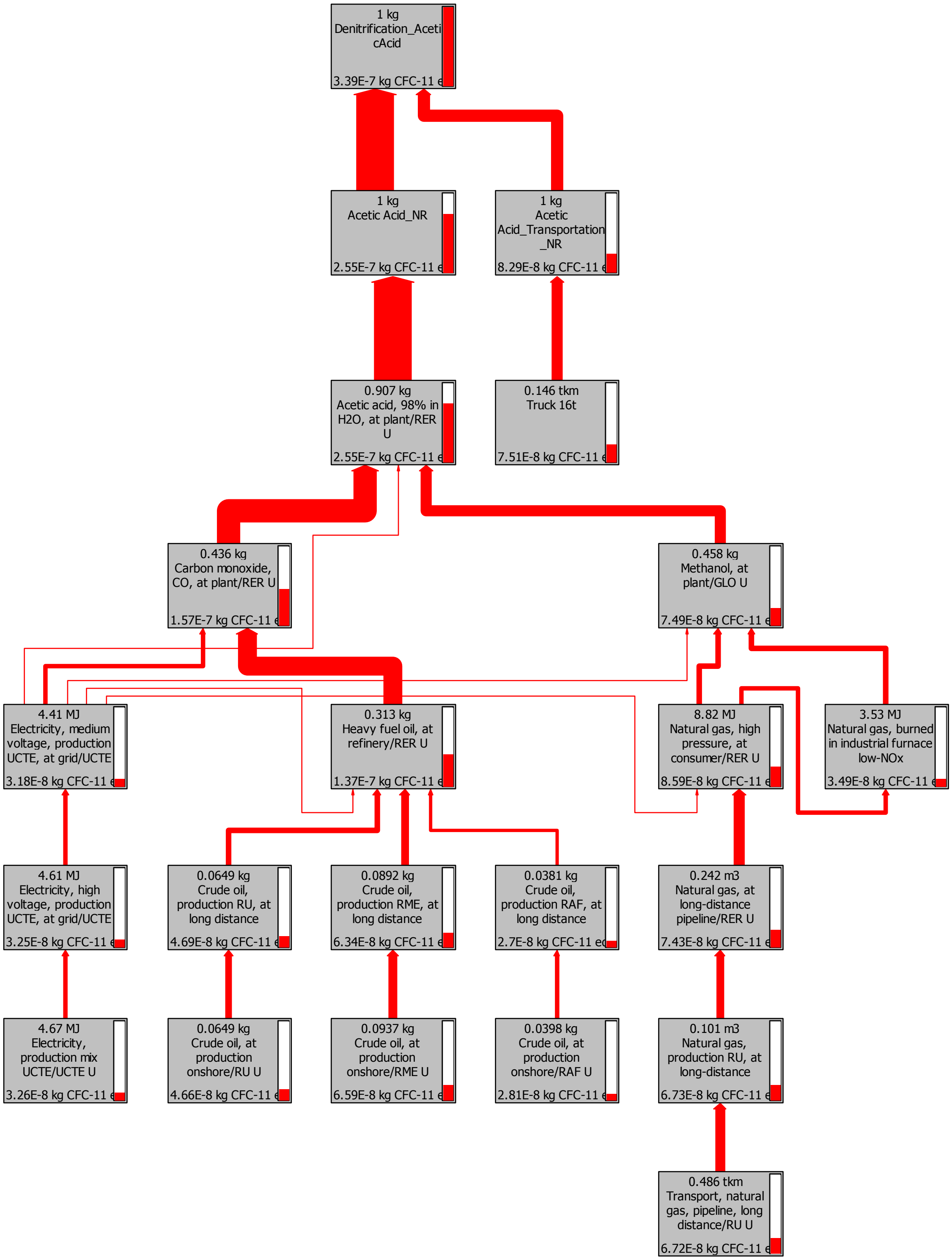

Figure A-7. Flow diagram of acetic acid for ozone depletion impacts

In utilizing acetic acid for denitrification, the impact in terms of eco-toxicity is due mainly to acetic acid production with a small portion of the impact from filter operation (Figure A-8).

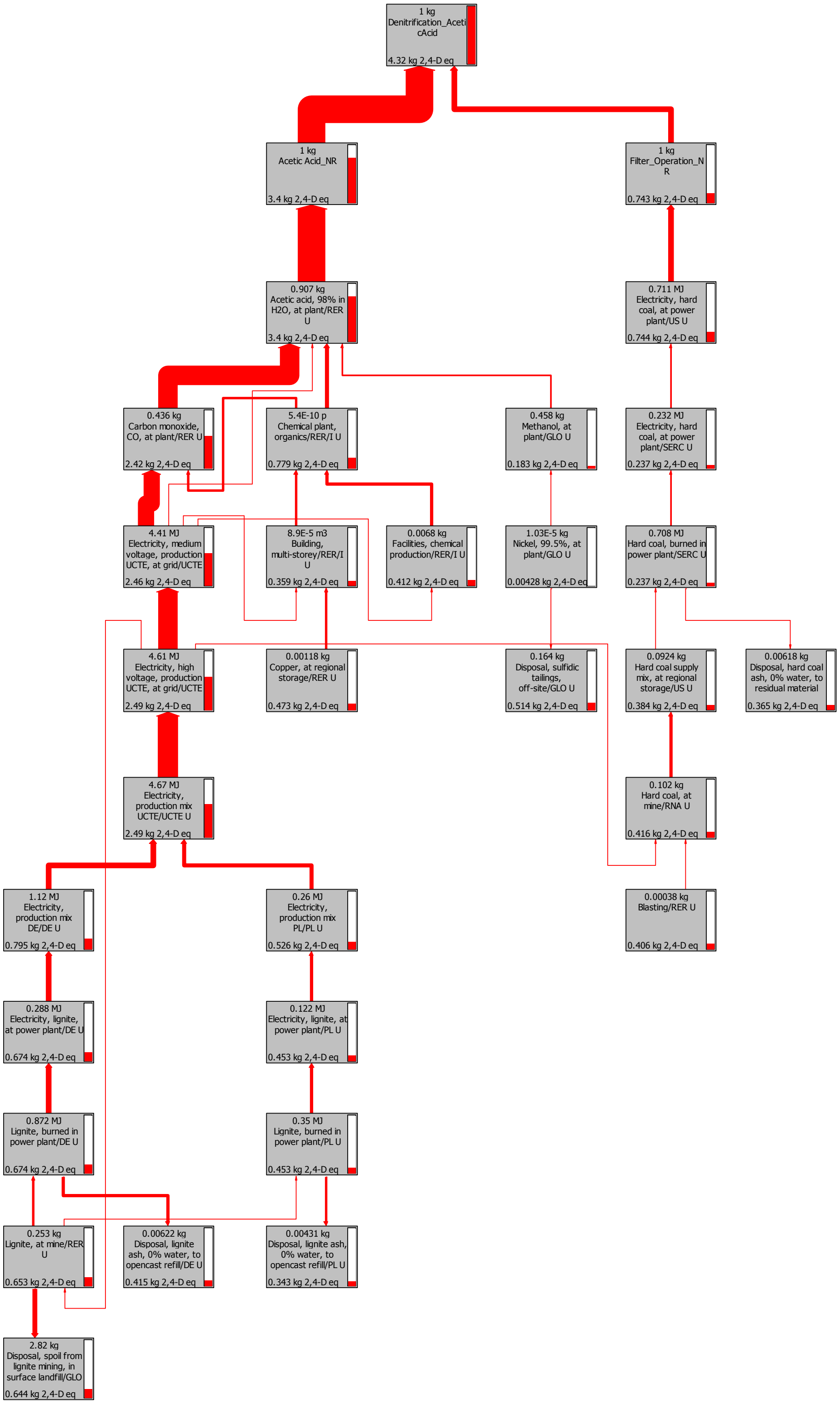

Figure A-8. Flow diagram of acetic acid for eco-toxicity impacts

In utilizing acetic acid for denitrification, the impact in terms of smog is due mainly to acetic acid production with a small portion of the impact from transportation and filter operation (Figure A-9).

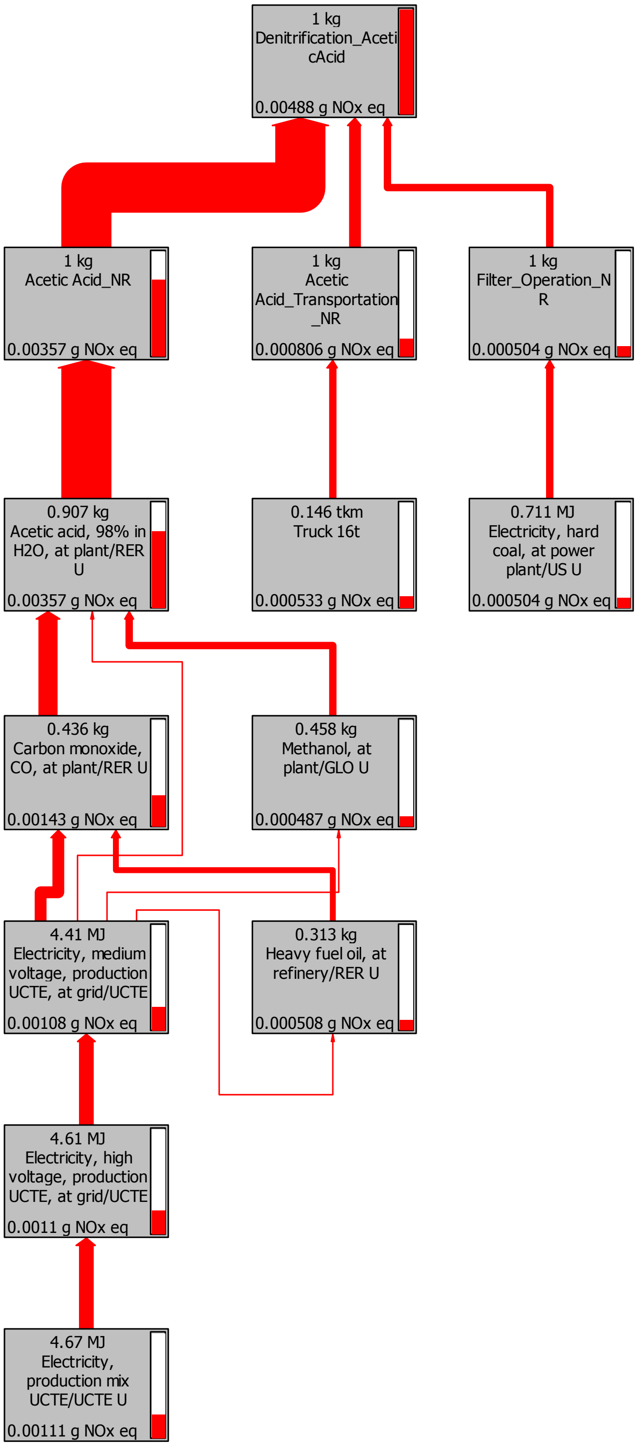

Figure A-9. Flow diagram of acetic acid for smog impacts

In utilizing methanol for denitrification, the impact in terms of global warming is due mainly to methanol production with a small portion from filter operation (Figure A-10).

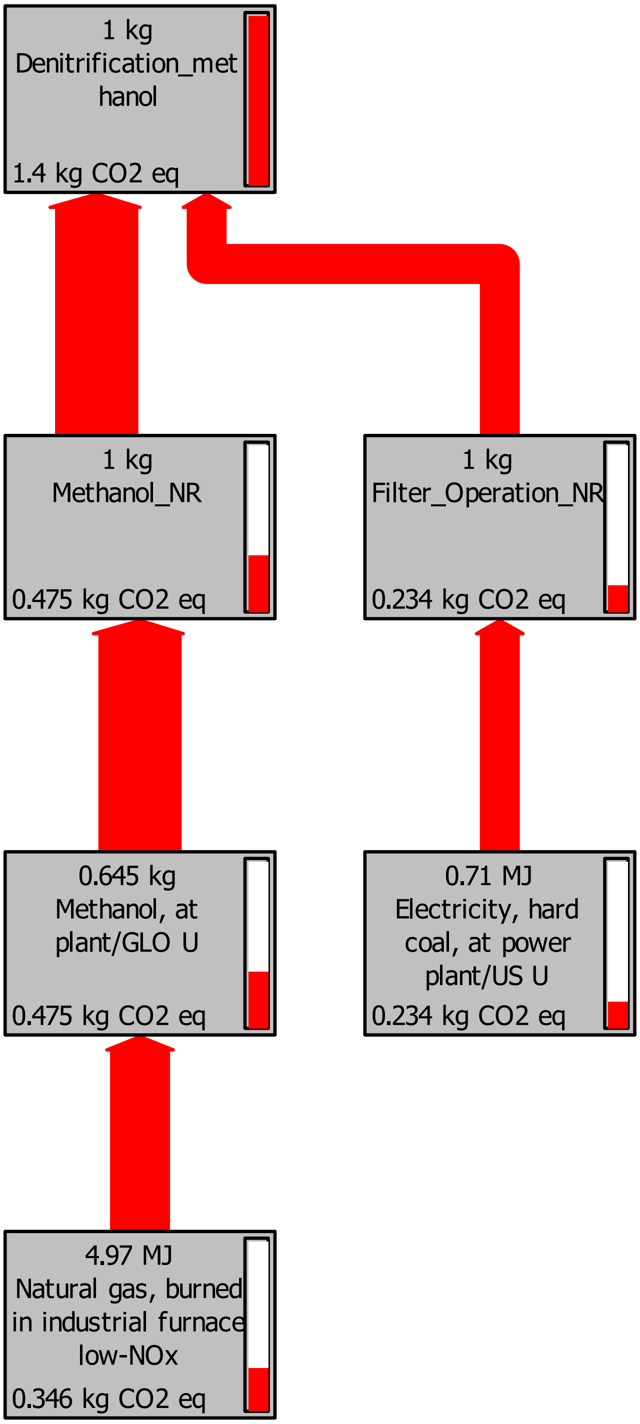

Figure A-10. Flow diagram of methanol for global warming impacts

In utilizing methanol for denitrification, the impact in terms of acidification is due mainly to filter operation with smaller contributions from methanol manufacture and transport (Figure A-11).

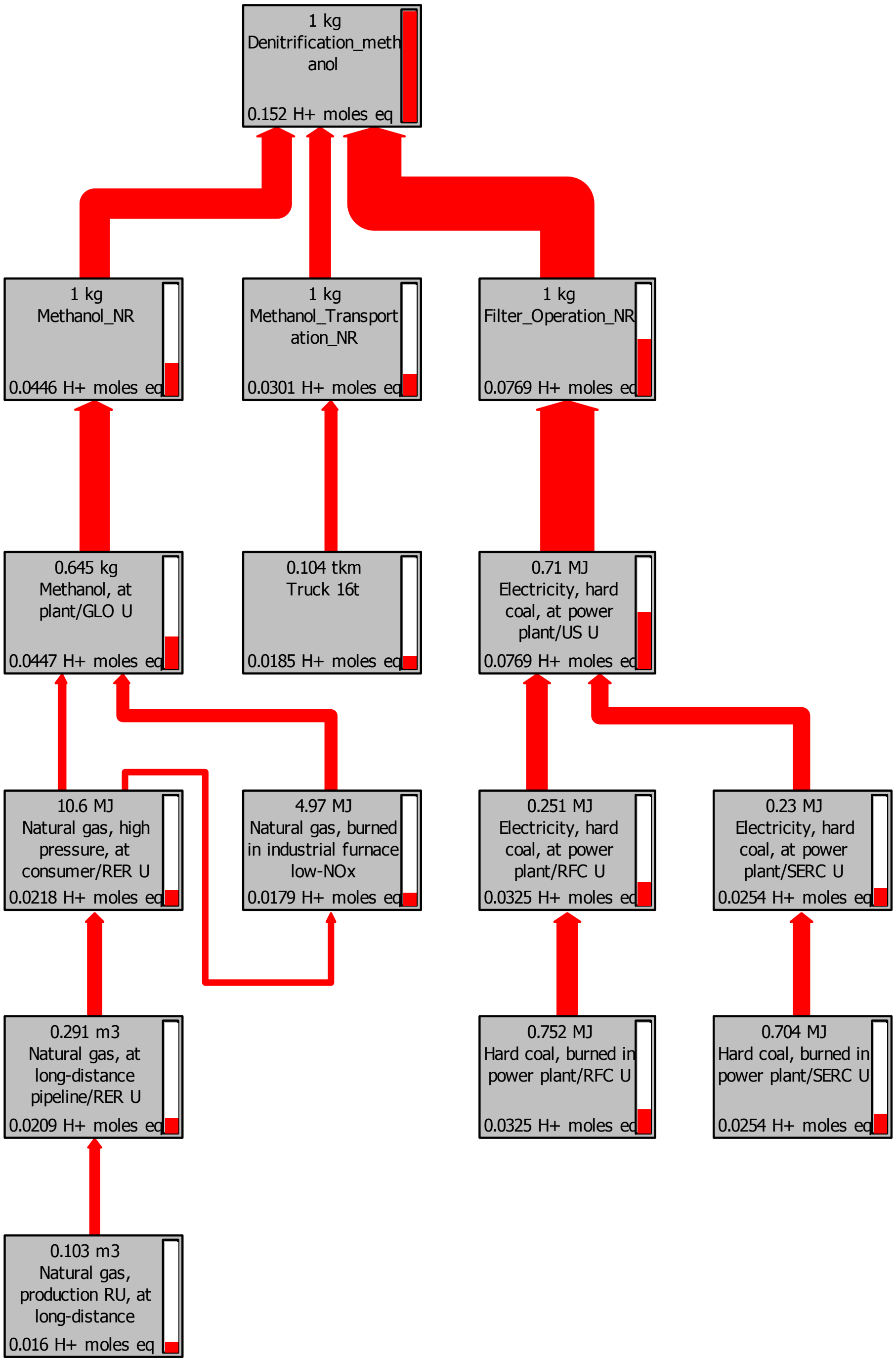

Figure A-11. Process flow diagram of methanol for acidification impacts

In utilizing methanol for denitrification, the impact in terms of carcinogens is due mainly to filter operation with smaller contributions from methanol manufacture and transport (Figure A-12).

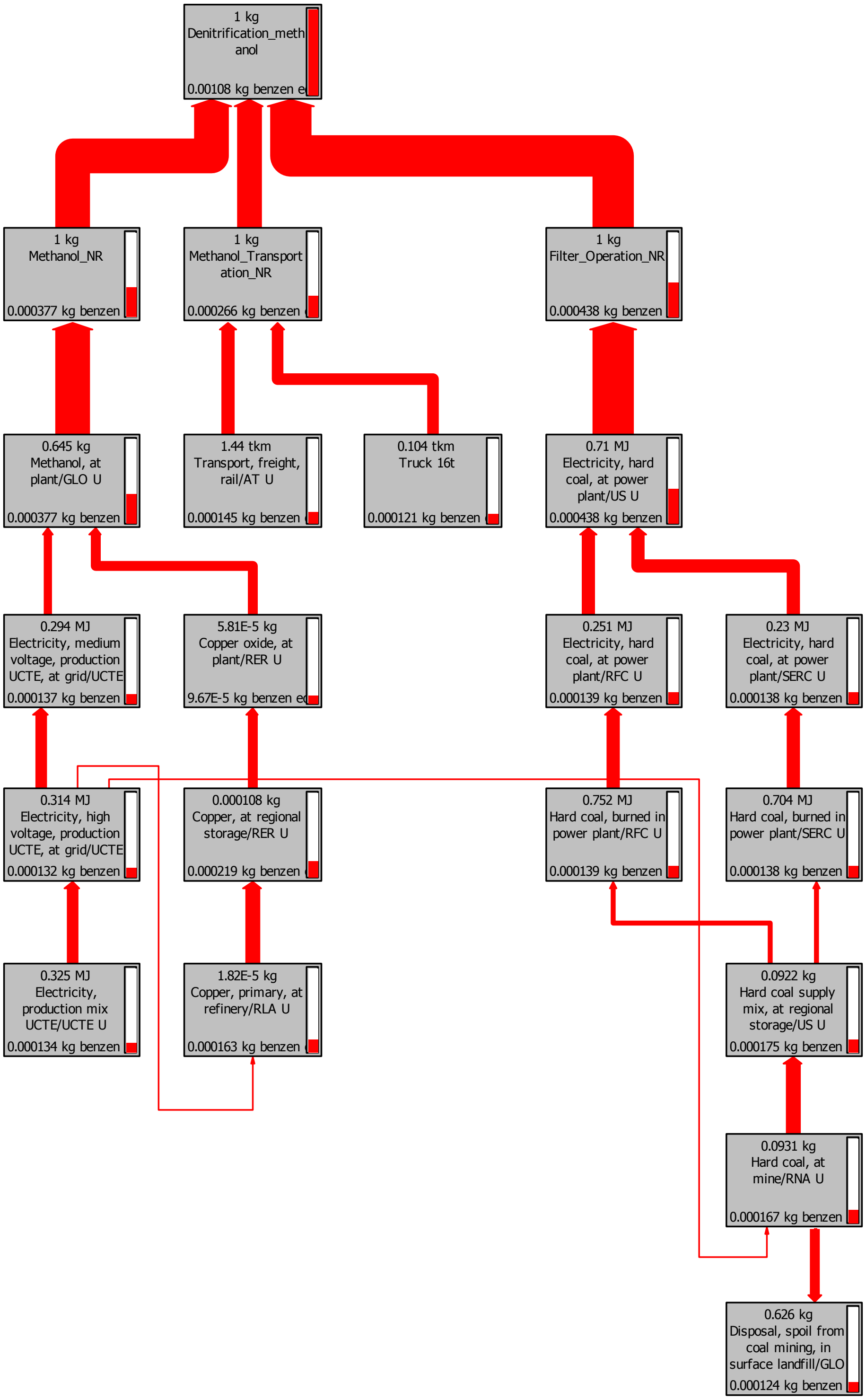

Figure A-12. Process flow diagram of methanol for carcinogenic impacts

In utilizing methanol for denitrification, the impact in terms of non-carcinogenic air pollutants is due mainly to methanol manufacture with smaller contributions from transport and filter operation (Figure A-13).

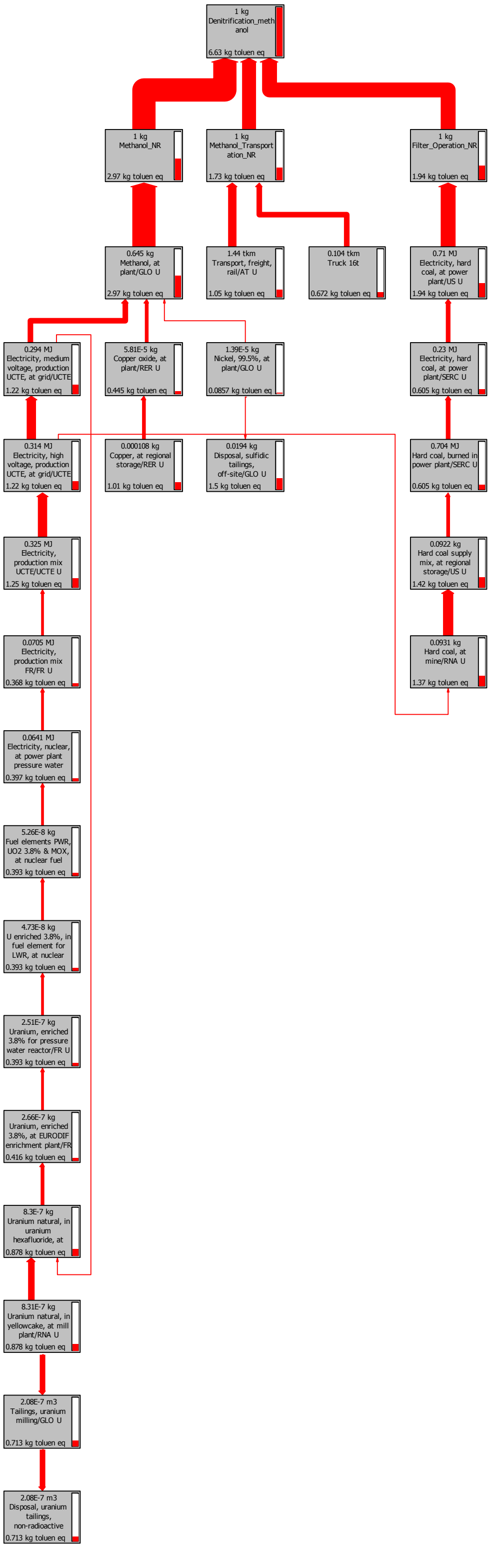

Figure A-13. Process flow diagram of methanol for non-carcinogenic impacts

In utilizing methanol for denitrification, the impact in terms of respiratory effects is due mainly to filter operation with smaller contributions from methanol manufacture and transport (Figure A-14).

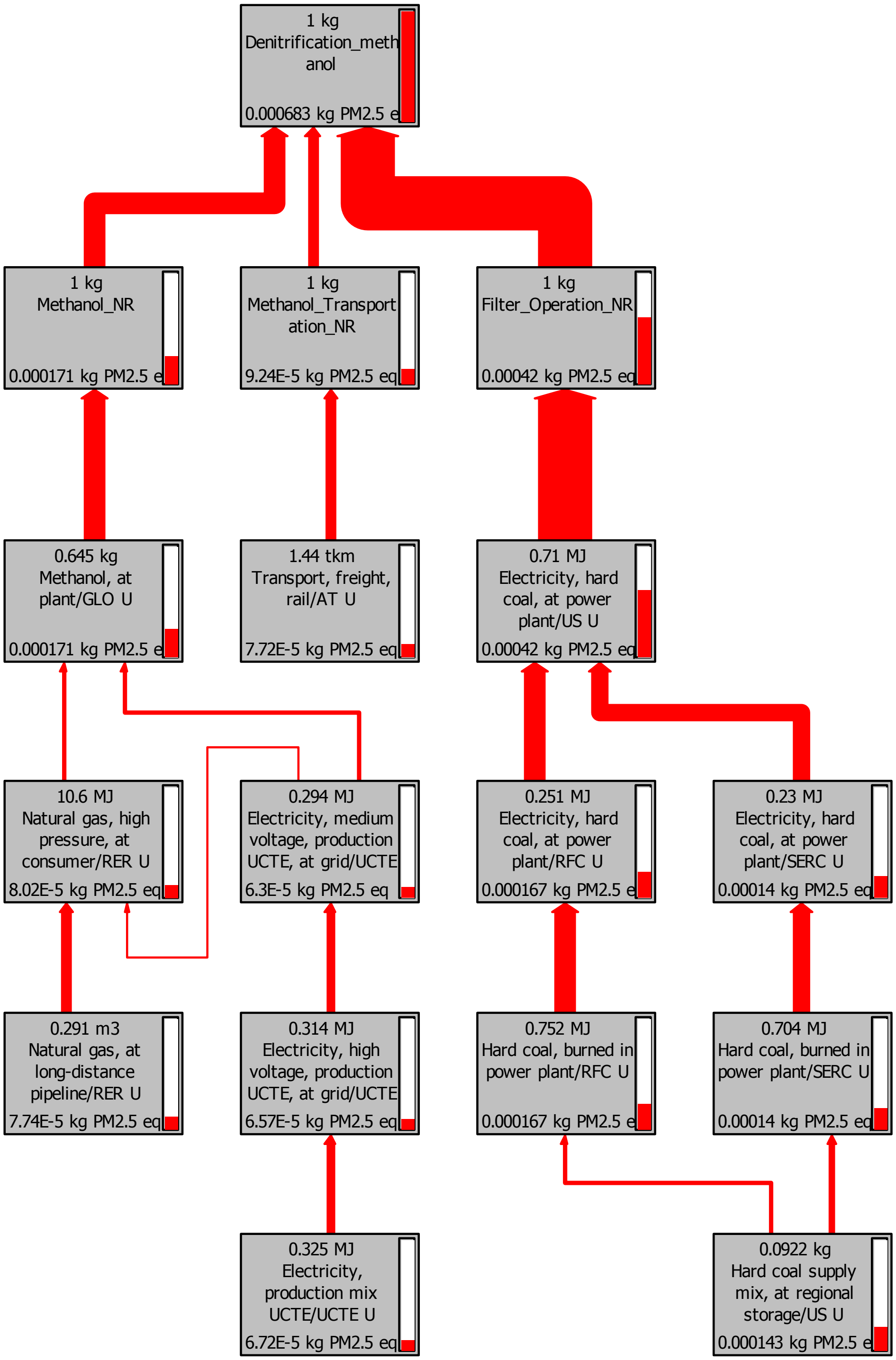

Figure A-14. Process flow diagram of methanol for respiratory effects impacts

In utilizing methanol for denitrification, the impact in terms of eutrophication is negative, hence the green arrow (Figure A-15). This is due to the fact that there are no large eutrophication impacts due to the use of methanol for denitrification, which means that this is a negative impact.

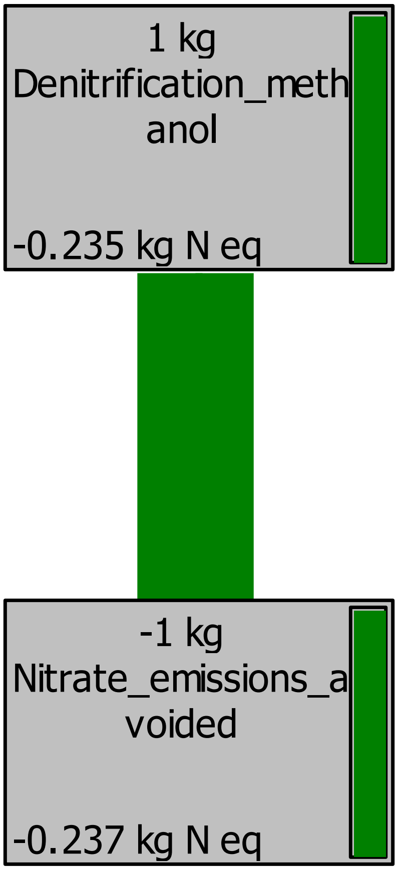

Figure A-15. Process flow diagram of methanol for eutrophication impacts

In utilizing methanol for denitrification, the impact in terms of ozone depletion is due mainly to methanol production with a smaller contribution from transport (Figure A-16).

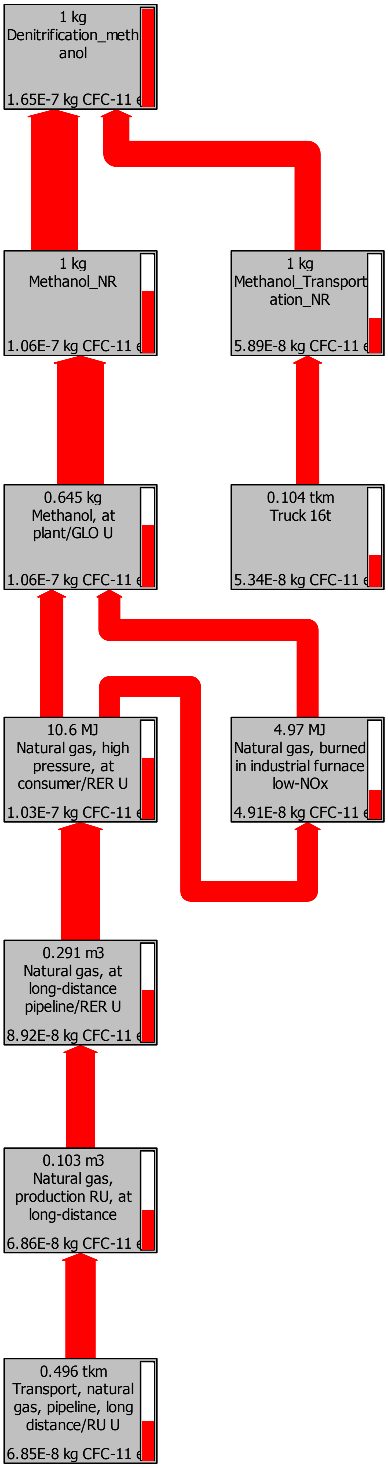

Figure A-16. Process flow diagram of methanol for ozone depletion impacts

In utilizing methanol for denitrification, the impact in terms of eco-toxicity is due mainly to filter operation with smaller contributions from methanol manufacture and transport (Figure A-17).

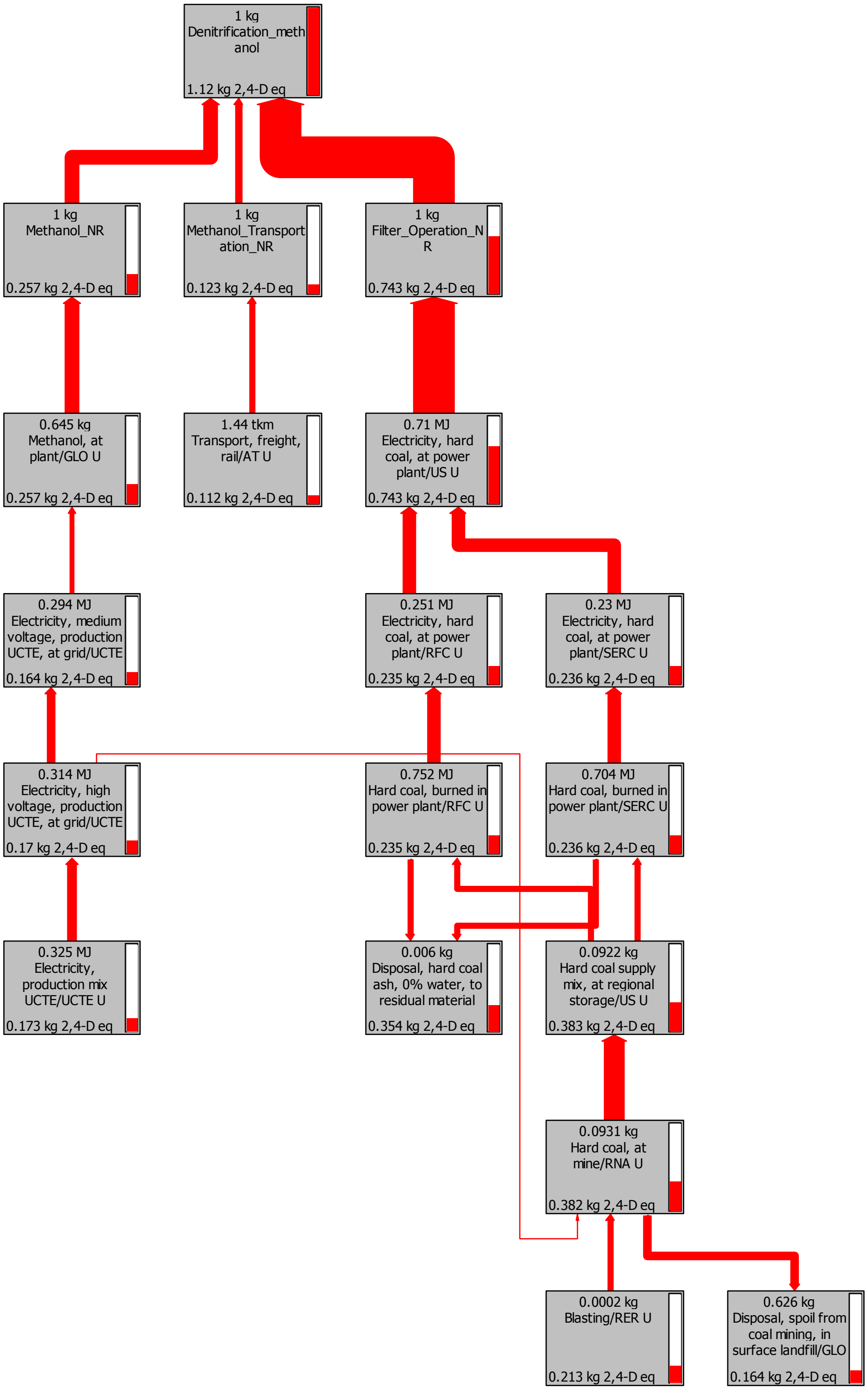

Figure A-17. Process flow diagram of methanol for eco-toxicity impacts

In utilizing methanol for denitrification, the impact in terms of smog is due mainly to methanol manufacture with smaller contributions from transport and filter operation (Figure A-18).

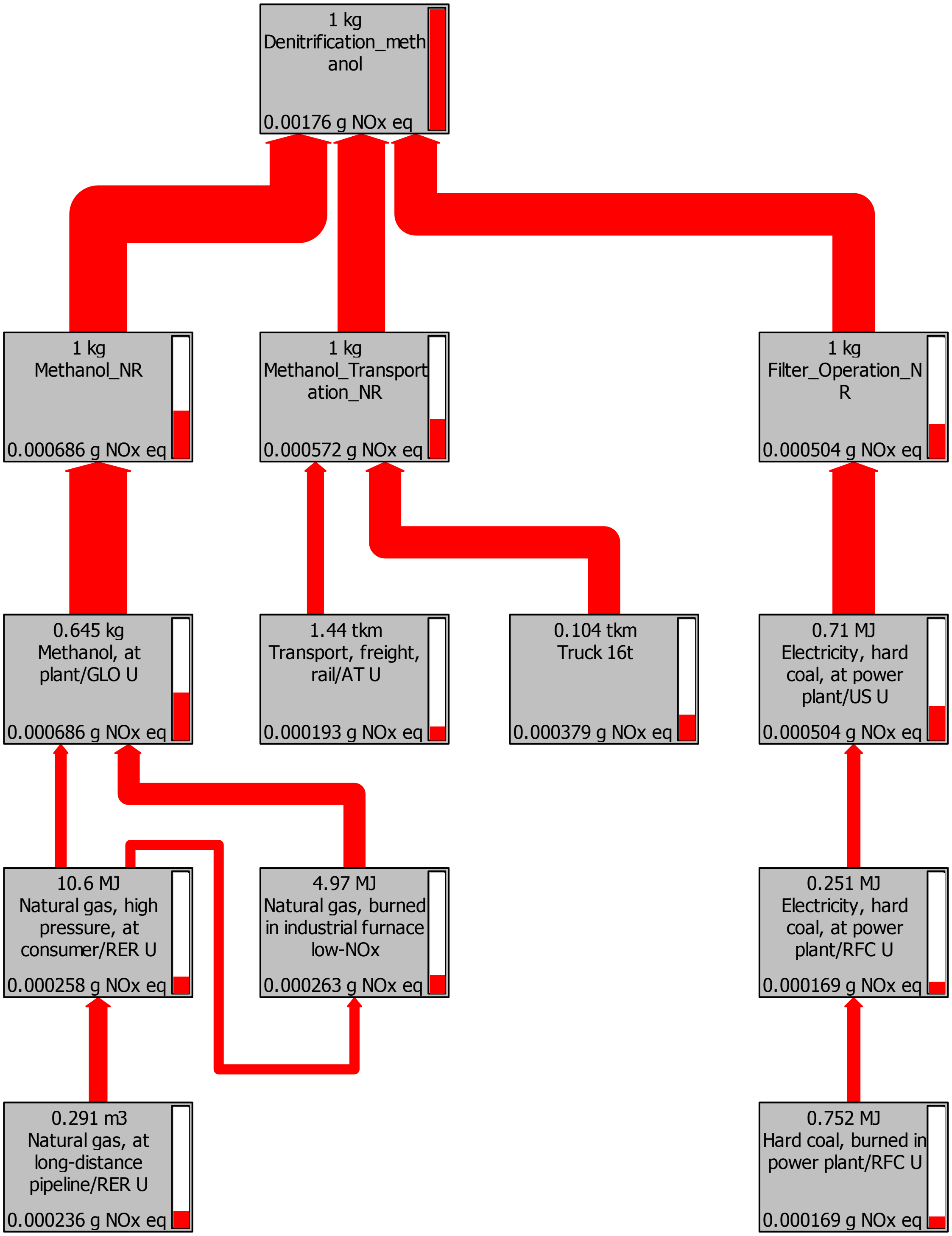

Figure A-18. Process flow diagram of methanol for smog impacts

In utilizing ethanol from corn for denitrification, the impact in terms of global warming is due mainly to ethanol manufacture with a smaller contribution from filter operation (Figure A-19).

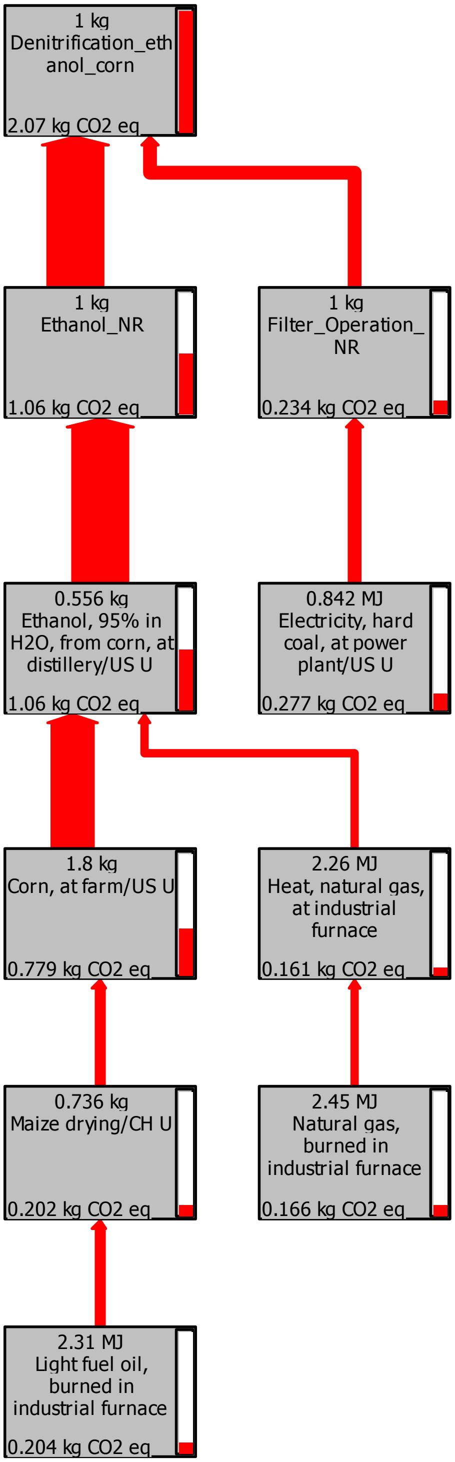

Figure A-19. Process flow diagram of ethanol from corn for global warming impacts

In utilizing ethanol from corn for denitrification, the impact in terms of acidification is due mainly to ethanol manufacture with a smaller contribution from filter operation (Figure A-20).

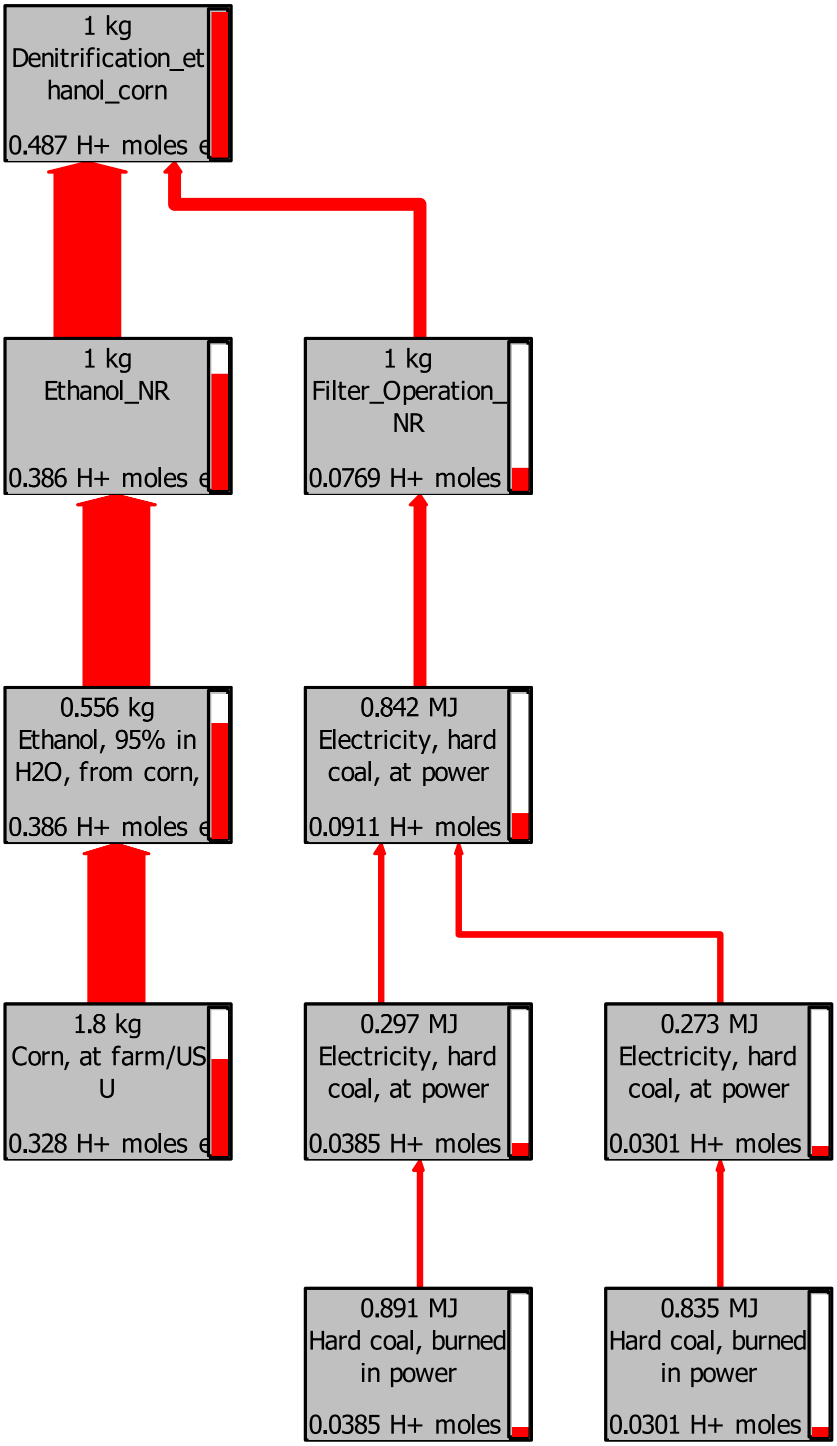

Figure A-20. Process flow diagram of ethanol from corn for acidification impacts

In utilizing ethanol from corn for denitrification, the impact in terms of carcinogenics is due mainly to ethanol manufacture with a smaller contribution from filter operation (Figure A-21).

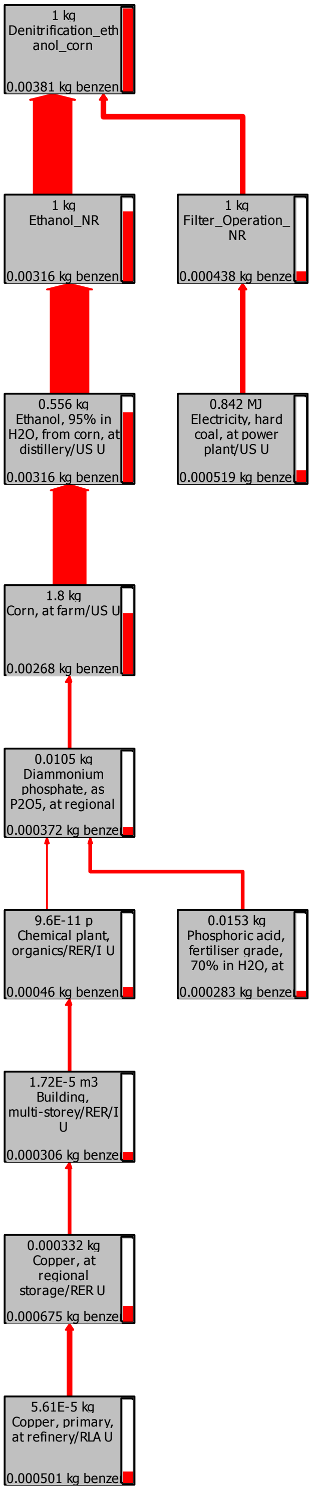

Figure A-21. Process flow diagram of ethanol from corn for carcinogenic impacts

In utilizing ethanol from corn for denitrification, the impact in terms of non-carcinogens is due mainly to ethanol manufacture with a smaller contribution from filter operation and transport (Figure A-22).

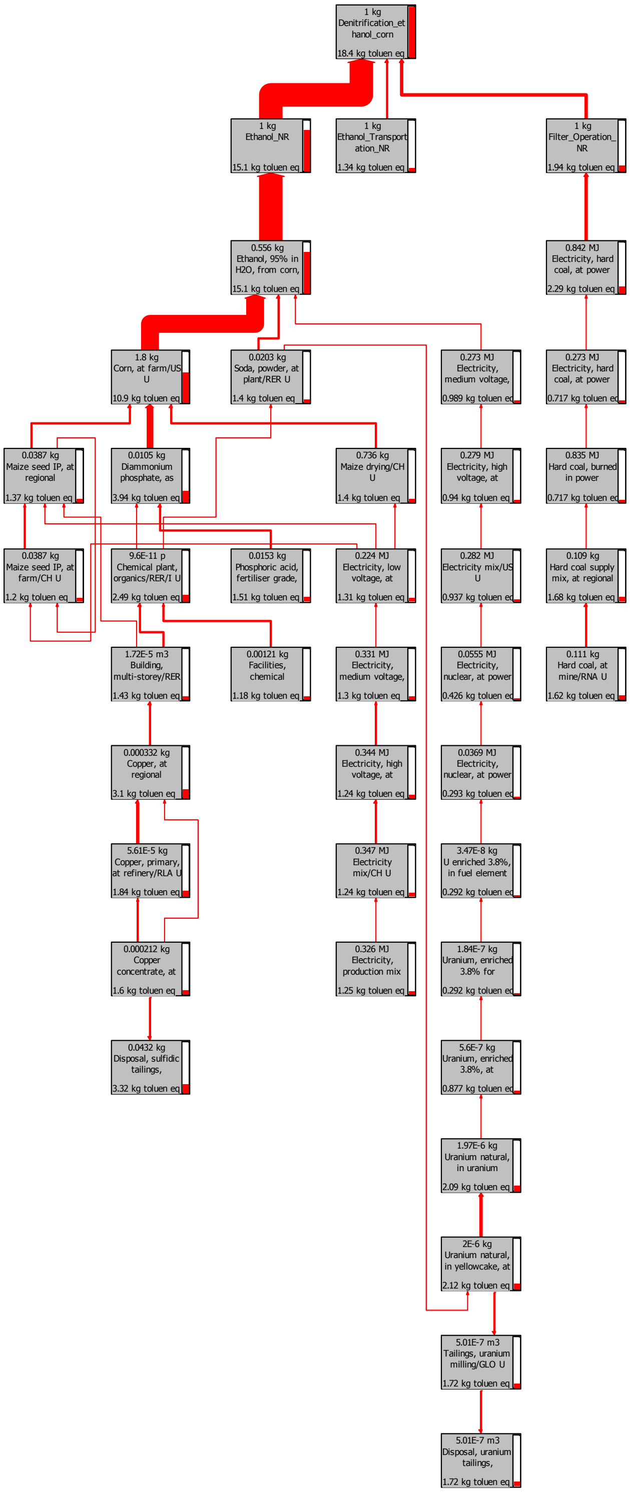

Figure A-22. Process flow diagram of ethanol from corn for non-carcinogenic impacts

In utilizing ethanol from corn for denitrification, the impact in terms of respiratory effects is due mainly to ethanol manufacture with a smaller contribution from filter operation (Figure A-23).

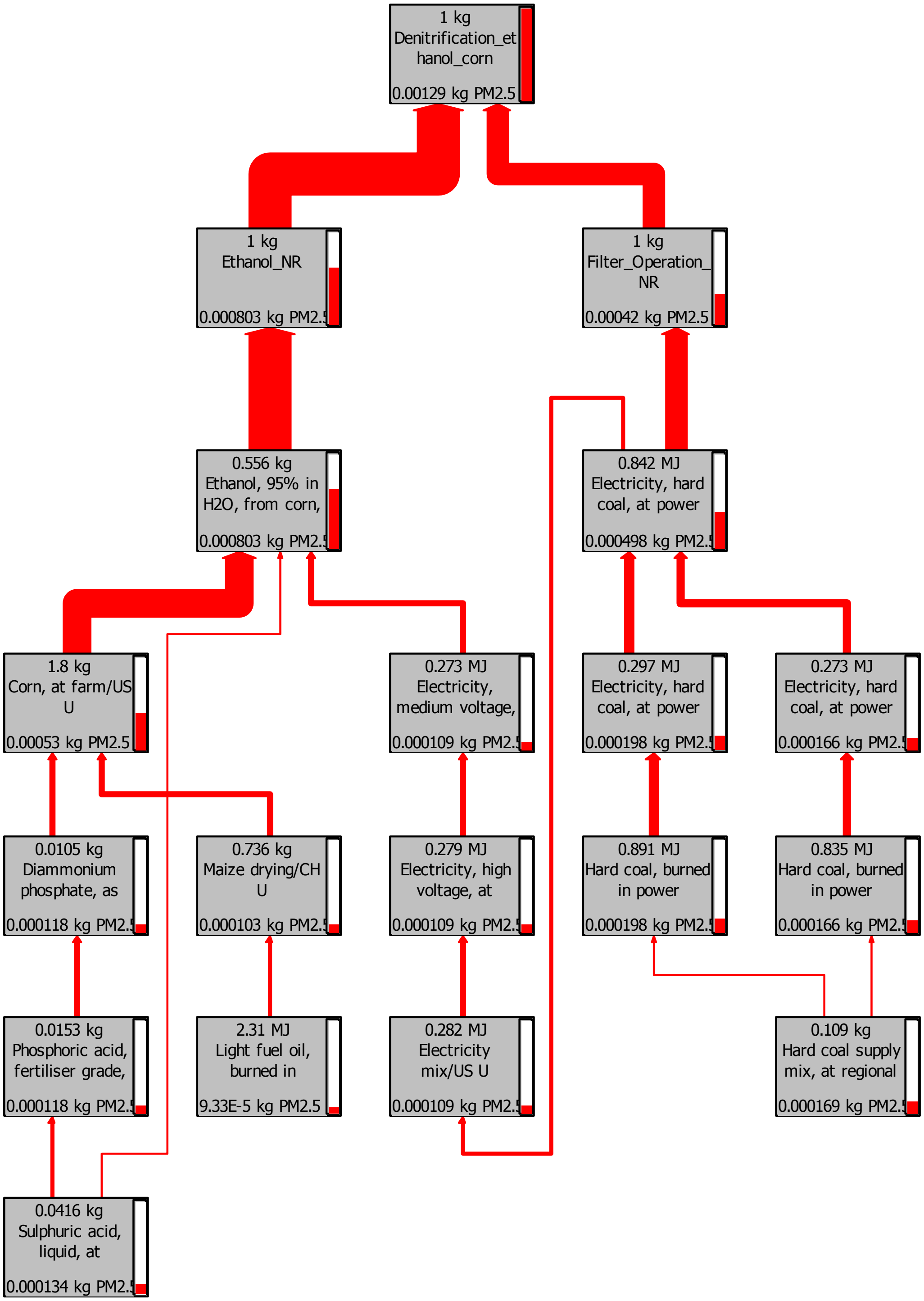

Figure A-23. Process flow diagram of ethanol from corm for respiratory effects impacts

In utilizing ethanol from corn for denitrification, the impact in terms of eutrophication is negative, hence the green arrow (Figure A-24). In manufacturing ethanol from corn, however, there are some positive effects contributing to the total impact, which is why there is also a red arrow.

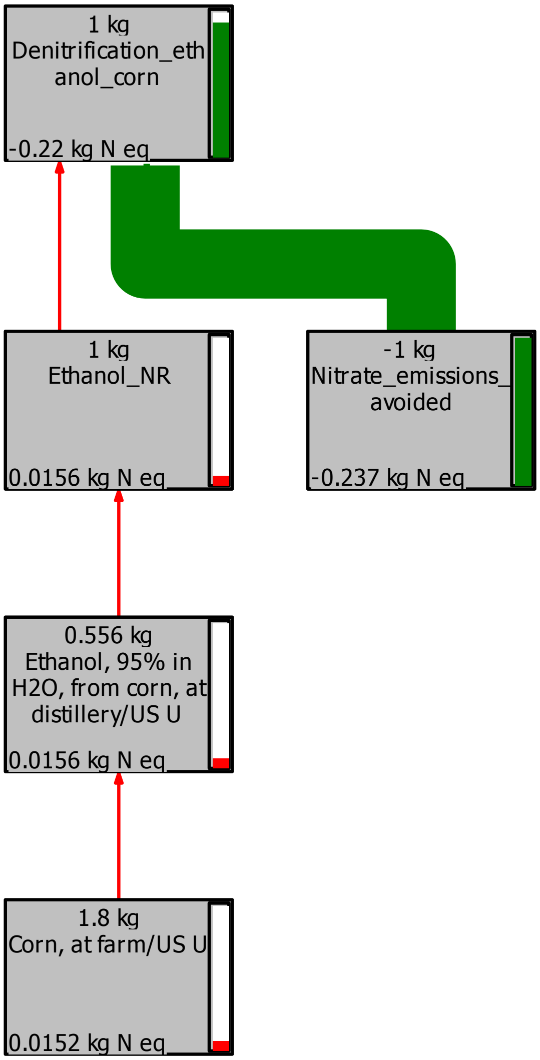

Figure A-24. Process flow diagram of ethanol from corn for eutrophication impacts

In utilizing ethanol from corn for denitrification, the impact in terms of ozone depletion the majority of the impact is due to ethanol manufacture with a smaller portion from transport (Figure A-25).

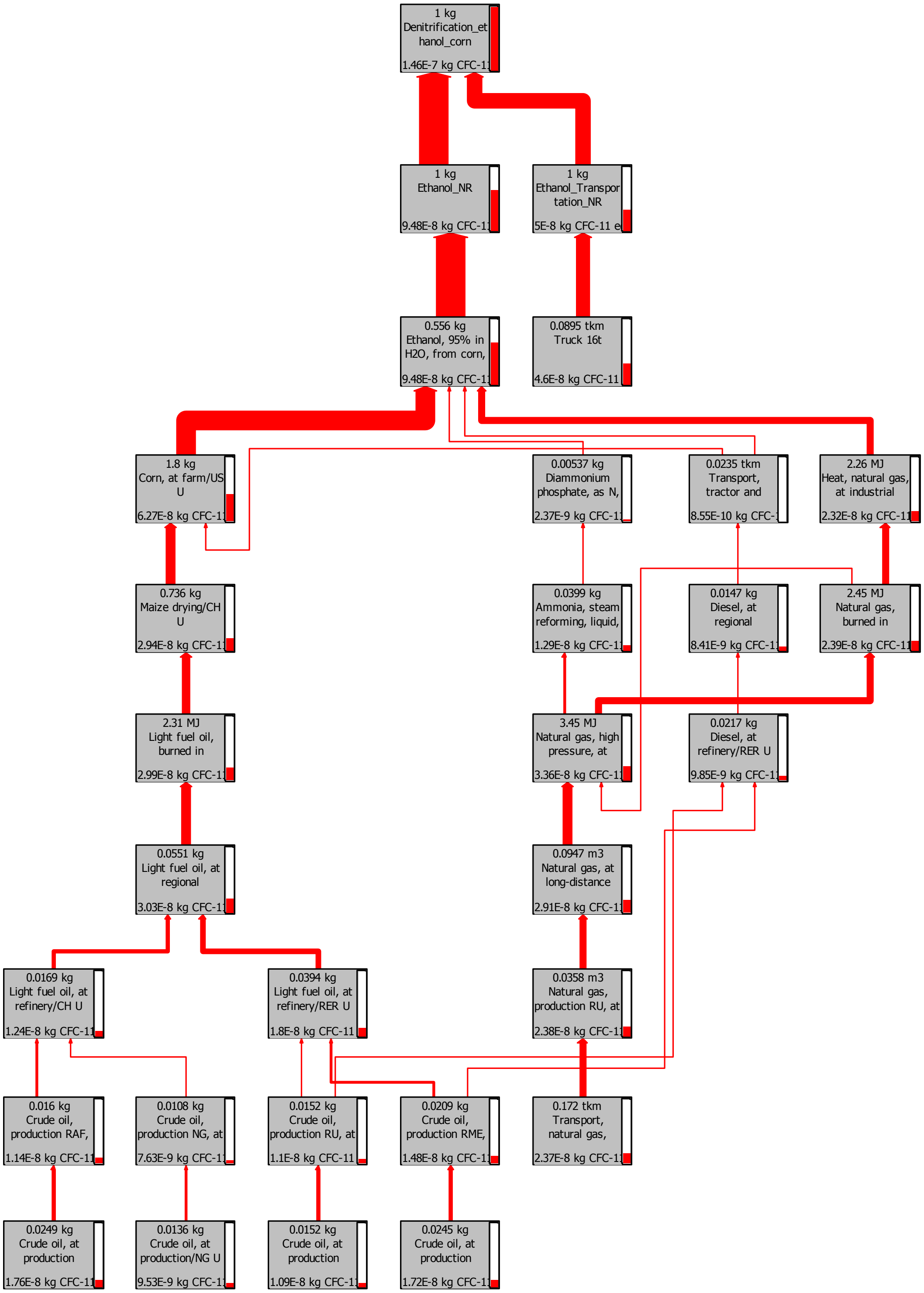

Figure A-25. Process flow diagram of ethanol from corn for ozone depletion impacts

In utilizing ethanol from corn for denitrification, the impact in terms of eco-toxicity the majority of the impact is due to filter operation with smaller portions from ethanol manufacture from corn and transport (Figure A-26).

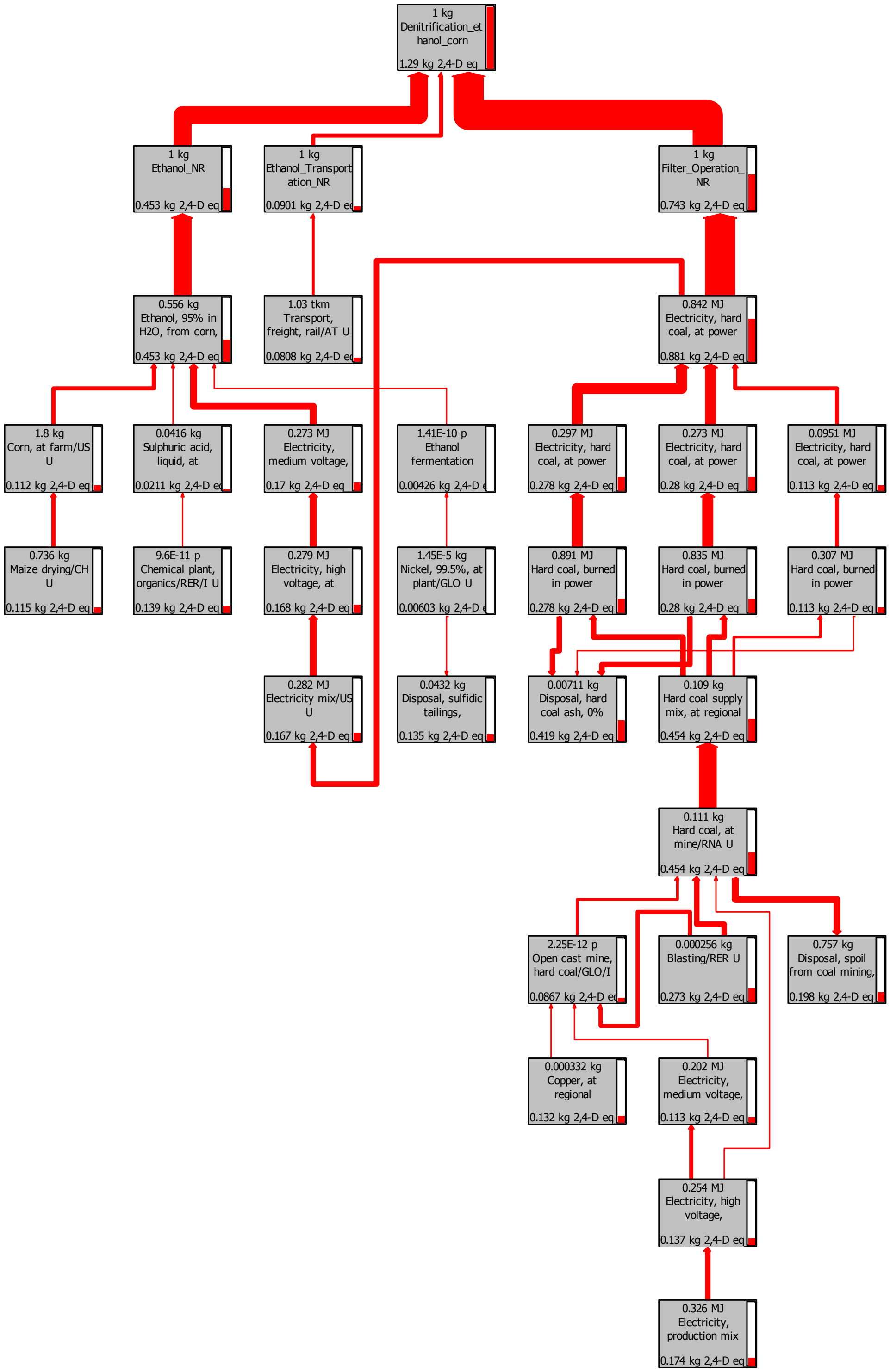

Figure A-26. Process flow diagram of ethanol from corn for eco-toxicity impacts

In utilizing ethanol from corn for denitrification, the impact in terms of smog the majority of the impact is due to ethanol production and smaller contributions due to transport and filter operation (Figure A-27).

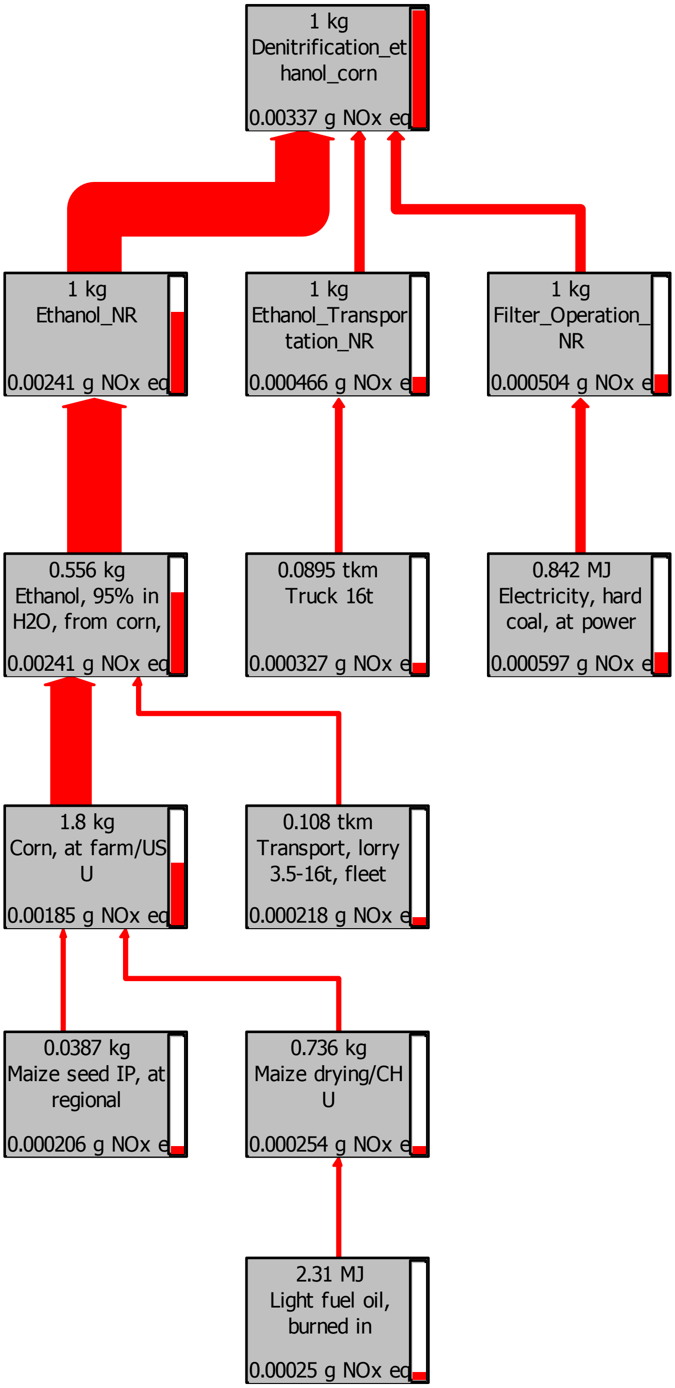

Figure A-27. Process flow diagram of ethanol from corn for smog impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of global warming is due mainly to ethanol manufacture and a smaller portion coming from filter operation and transport (Figure A-28).

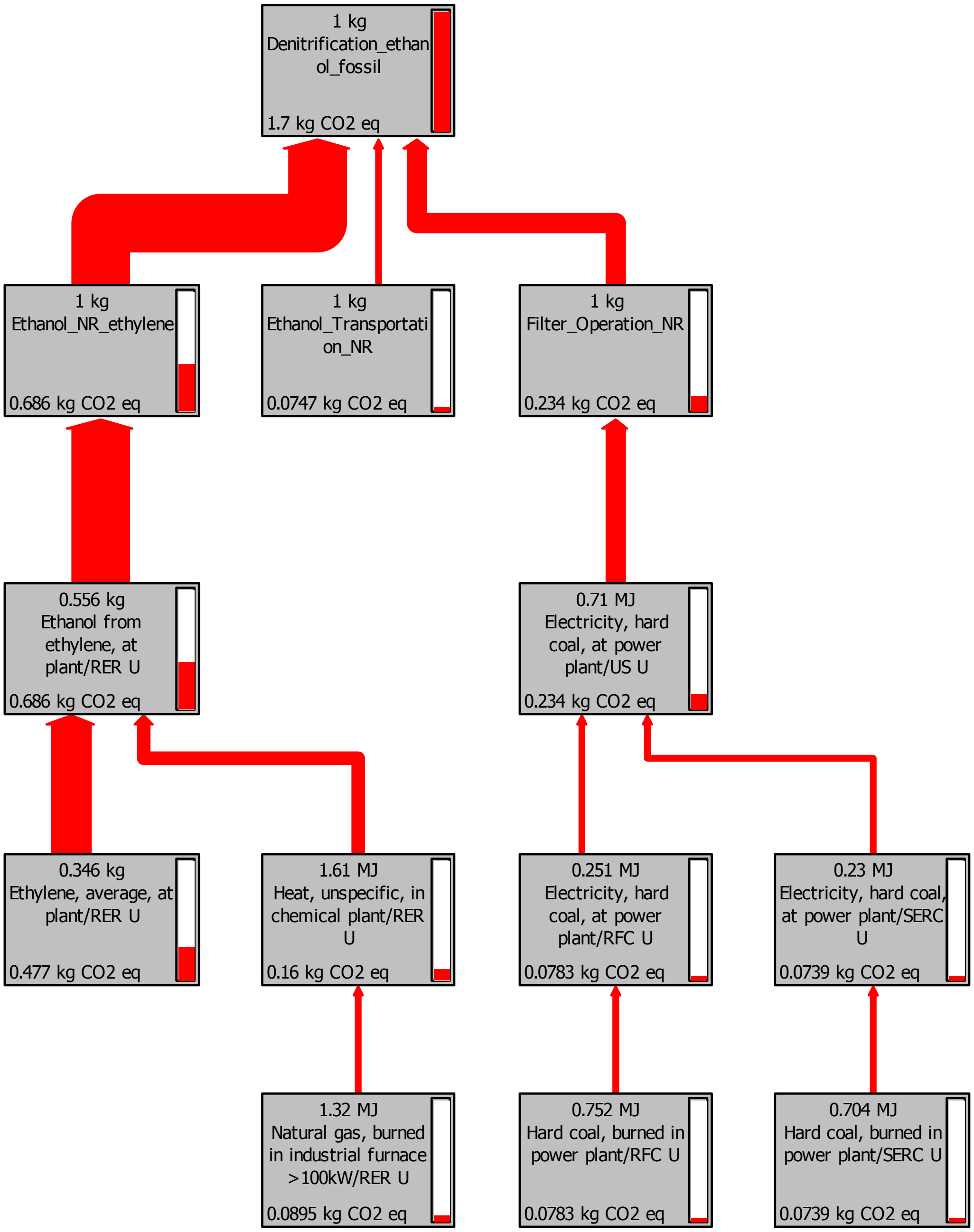

Figure A-28. Process flow diagram of ethanol from fossil sources for global warming impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of acidification is mainly due to ethanol manufacture and a smaller portion coming from filter operation and transport (Figure A-29).

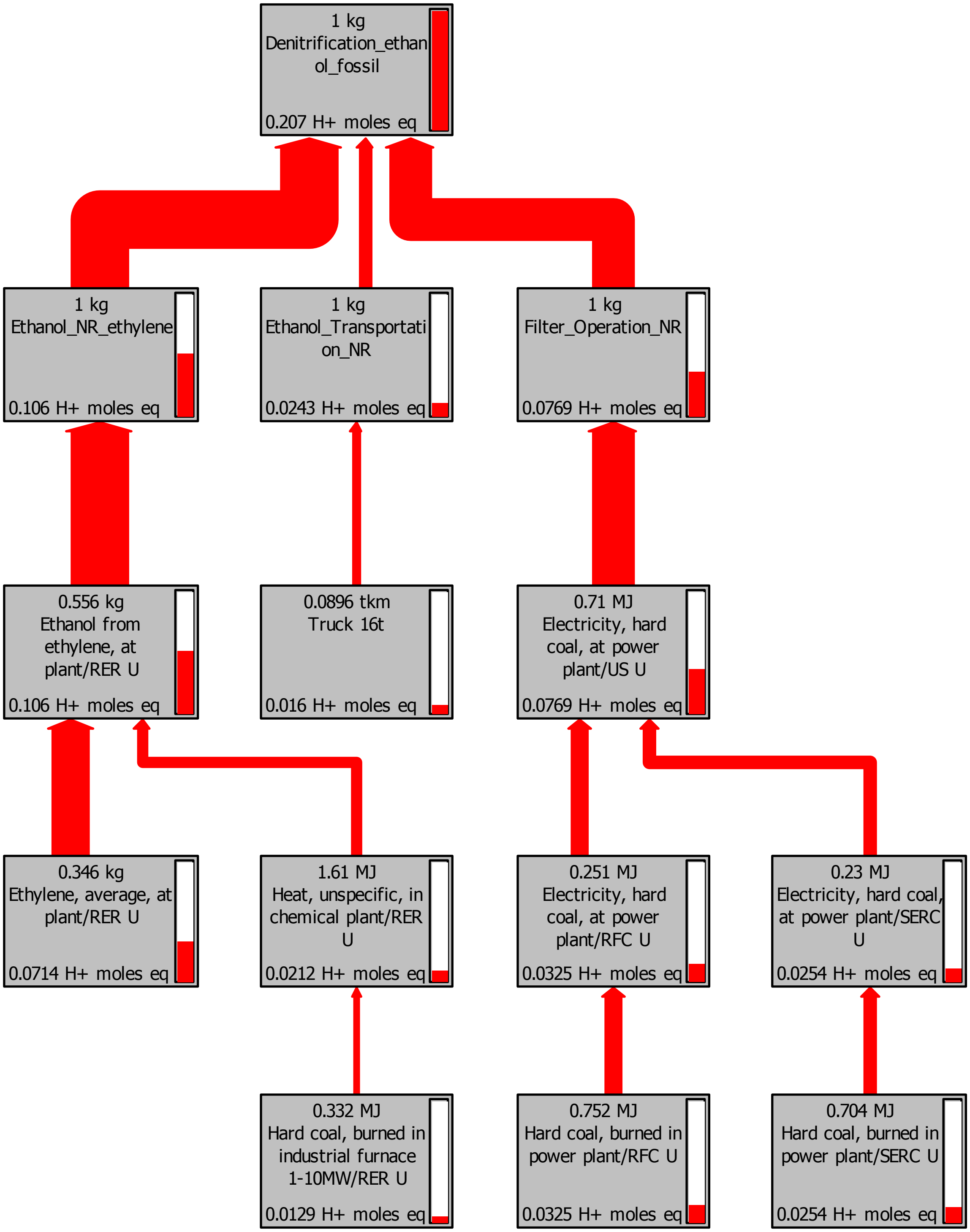

Figure A-29. Process flow diagrams of ethanol from fossil sources for acidification impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of carcinogenic emissions is mainly due to ethanol manufacture and a smaller portion coming from filter operation and transport (Figure A-30).

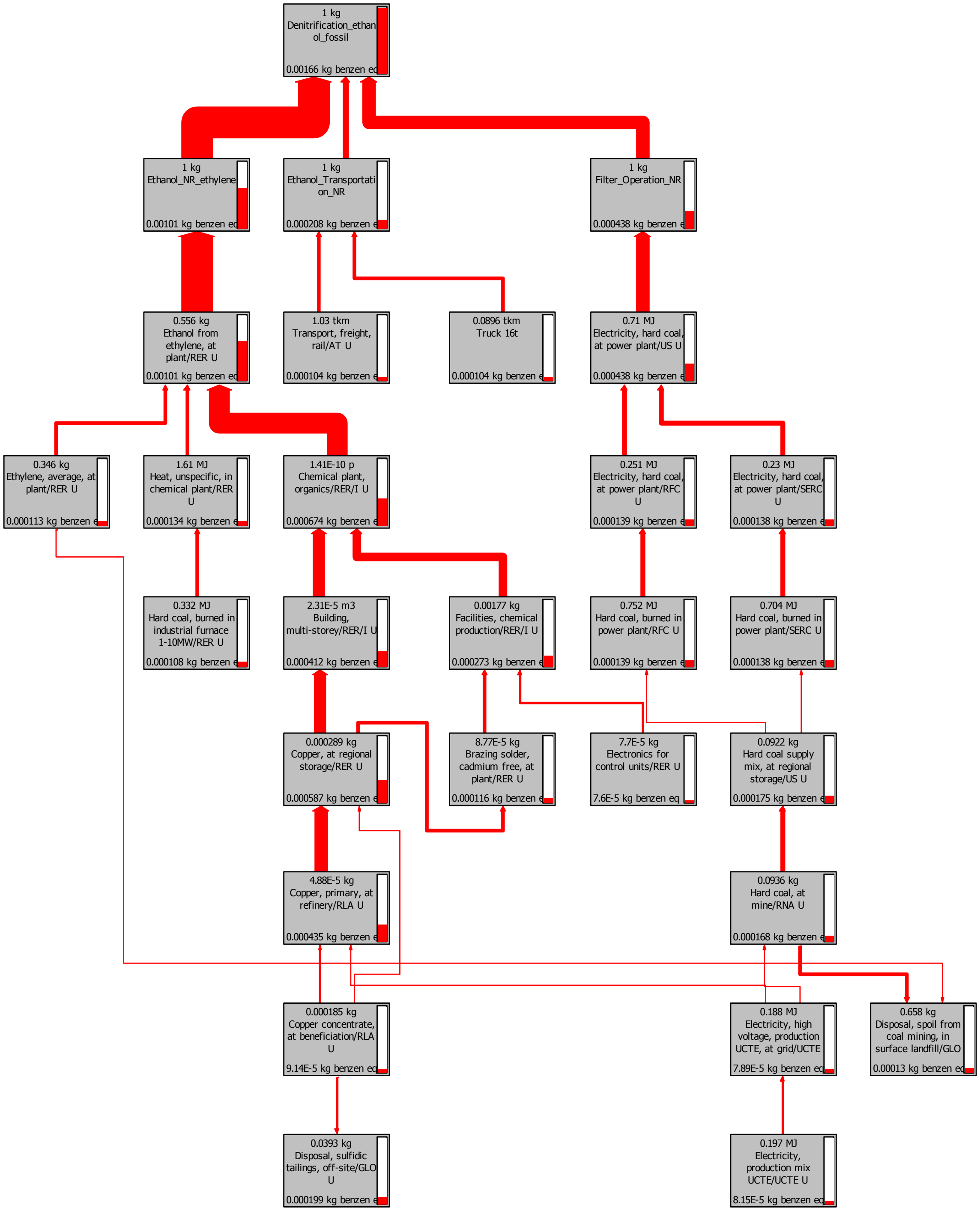

Figure A-30. Process flow diagram of ethanol from fossil sources for carcinogenic impacts

In utilizing ethanol from fossil soures for denitrification, the impact in terms of non-carcinogenics, is mainly due to ethanol manufacture with a smaller portion coming from filter operation and transport (Figure A-31).

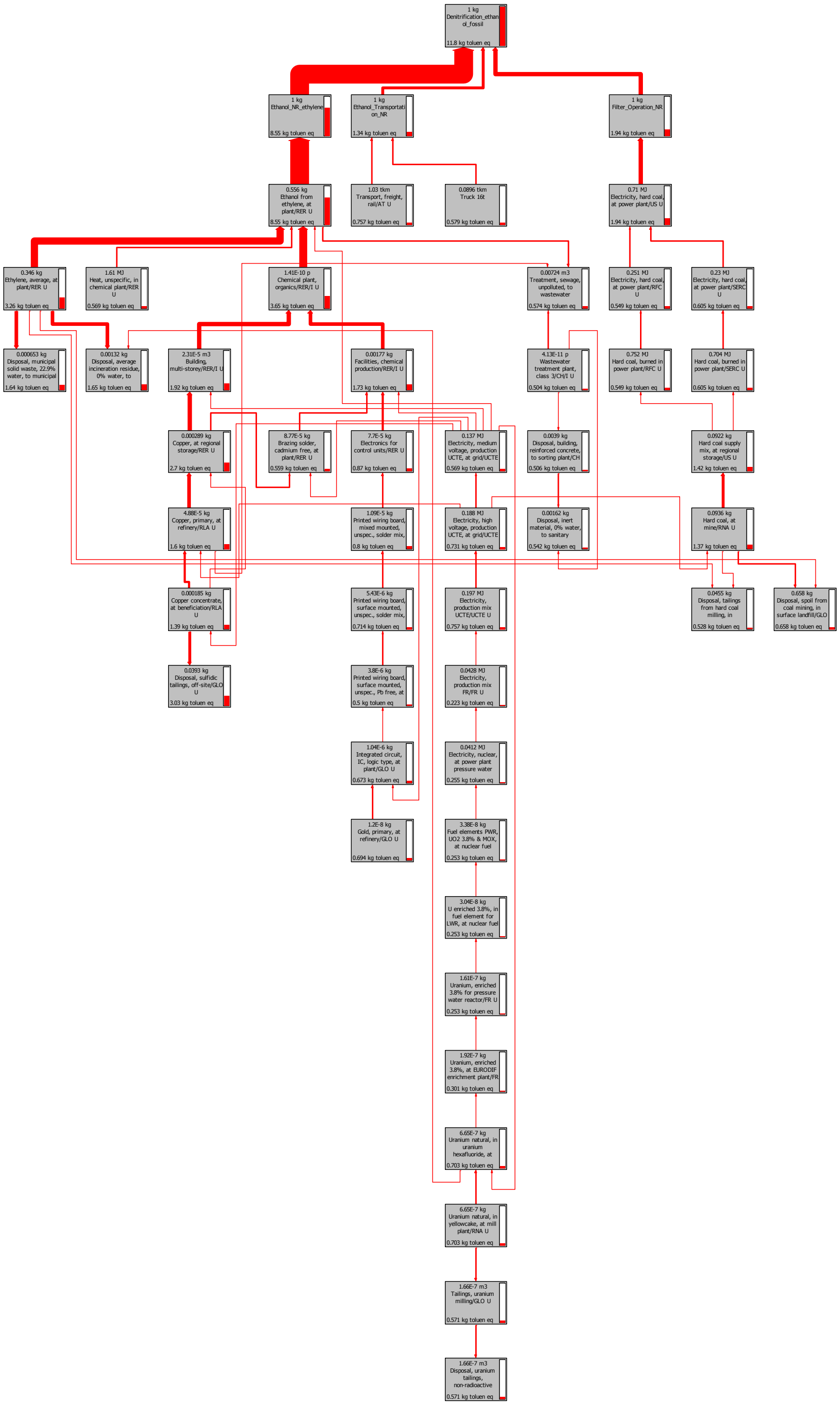

Figure A-31. Process flow diagram of ethanol from fossil sources for non-carcinogenic impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of respiratory effects is mainly due to ethanol manufacture and a smaller portion coming from filter operation and transport (Figure A-32).

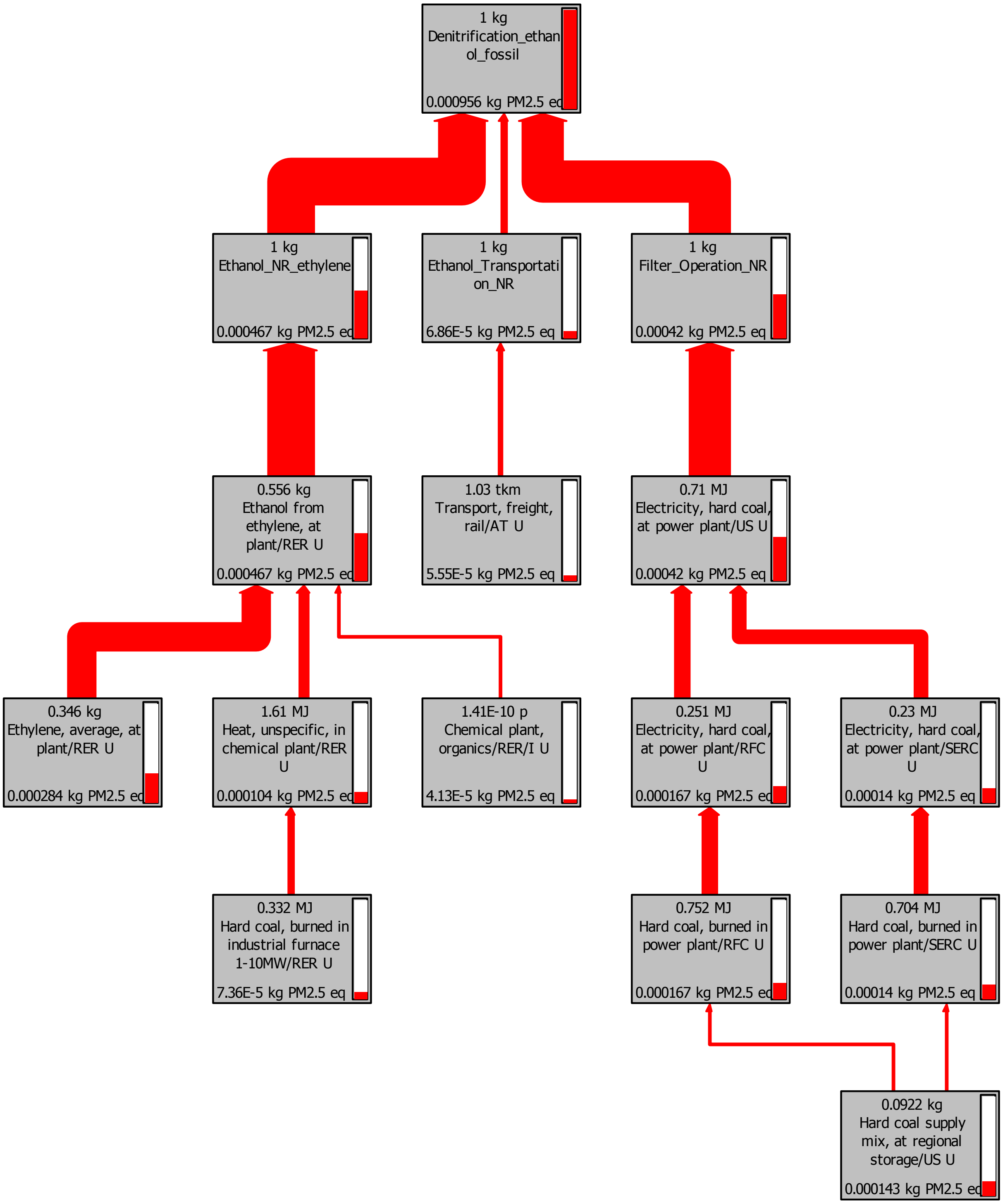

Figure A-32. Process flow diagram of ethanol from fossil sources for respiratory effects impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of eutrophication is negative, hence the green arrow (Figure A-33). This is due to the fact that there are no large eutrophication impacts due to the use of ethanol from fossil for denitrification, which means that this is a negative impact.

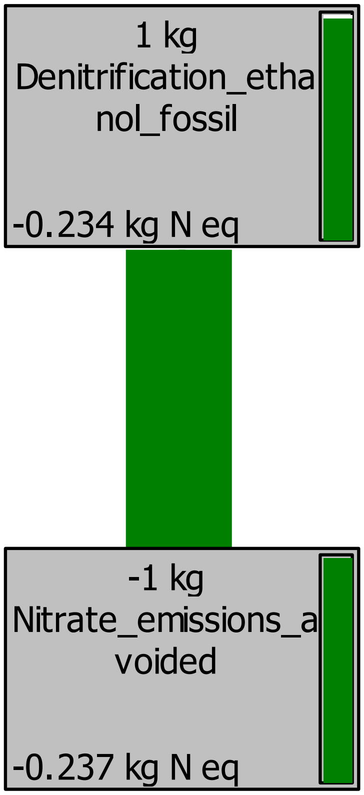

Figure A-33. Process flow diagrams of ethanol from fossil sources for eutrophication impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of ozone depletion the majority of the impact is due transport and a smaller portion from ethanol manufacture (Figure A-34).

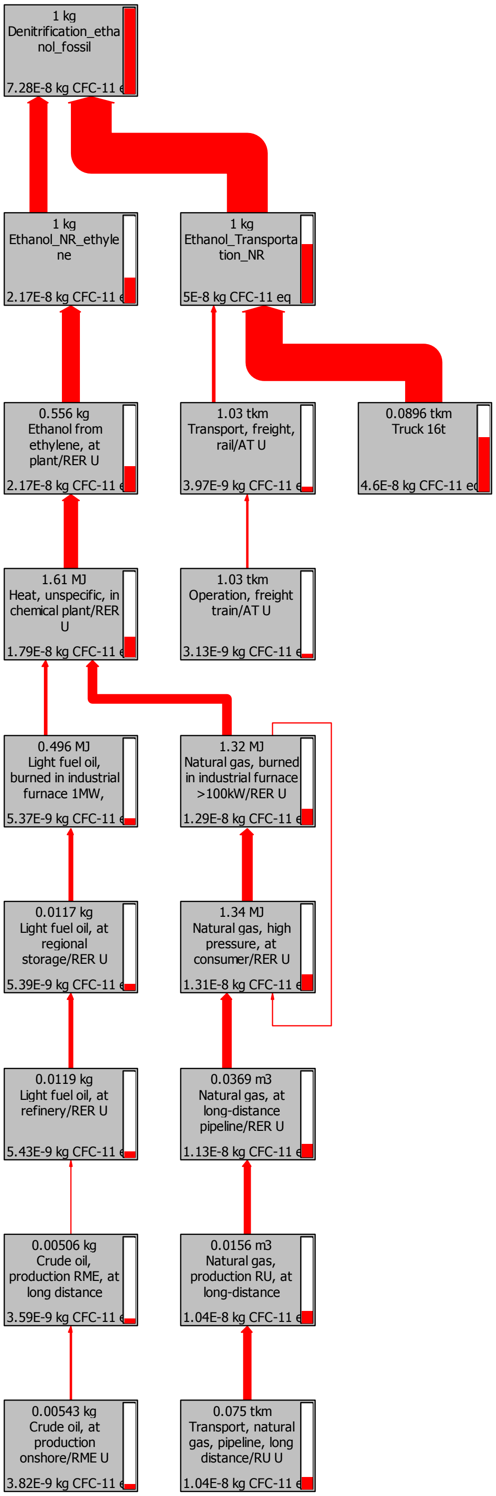

Figure A-34. Process flow diagram of ethanol from fossil sources for ozone depletion impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of eco-toxicity the majority of the impact is due filter operation with a smaller portion from ethanol manufacture and transport (Figure A-35).

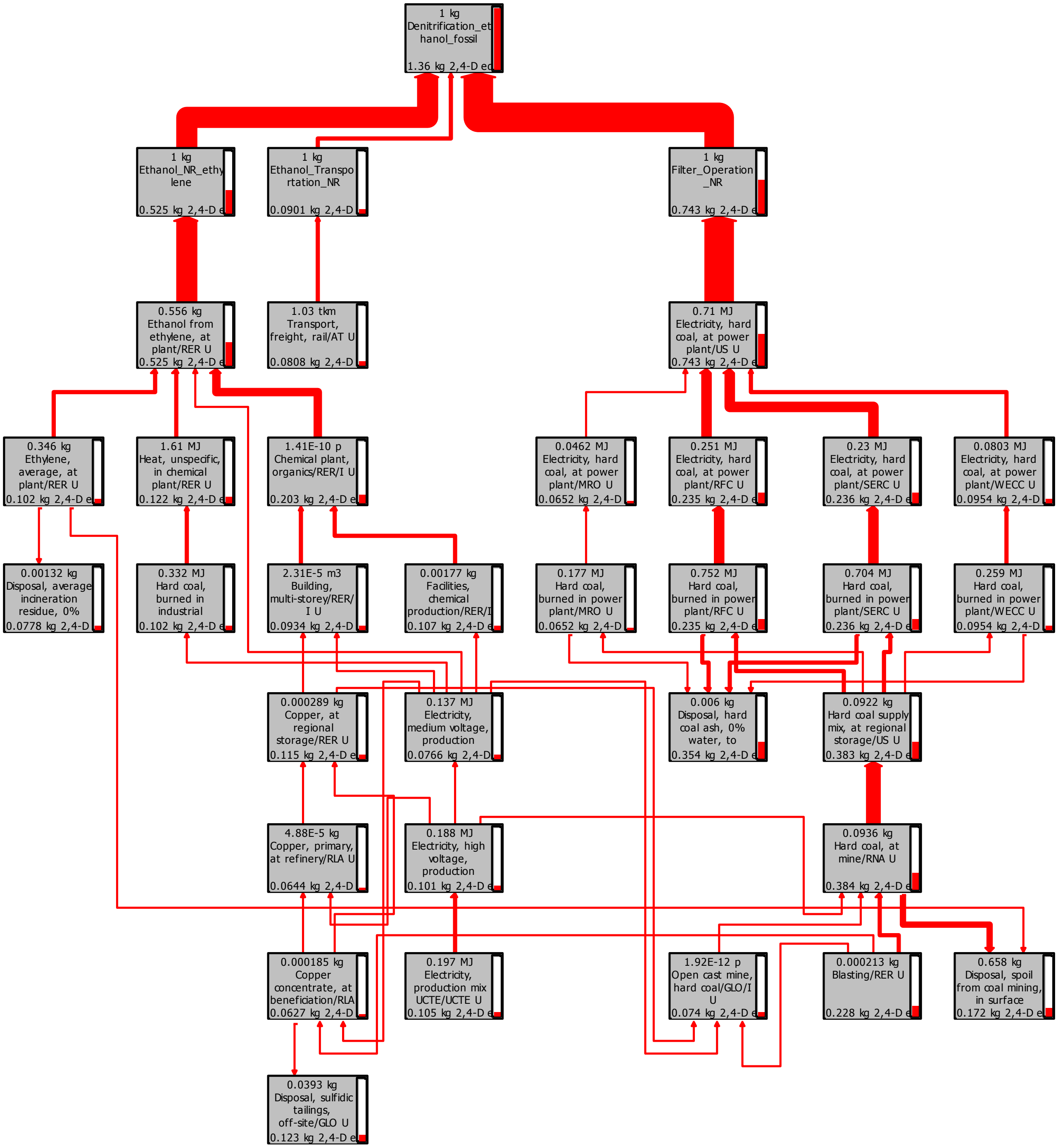

Figure A-35. Process flow diagram of ethanol from fossil sources for eco-toxicity impacts

In utilizing ethanol from fossil sources for denitrification, the impact in terms of eco-toxicity the majority of the impact is due ethanol manufacture with a smaller portion from transport and filter operation (Figure A-36).

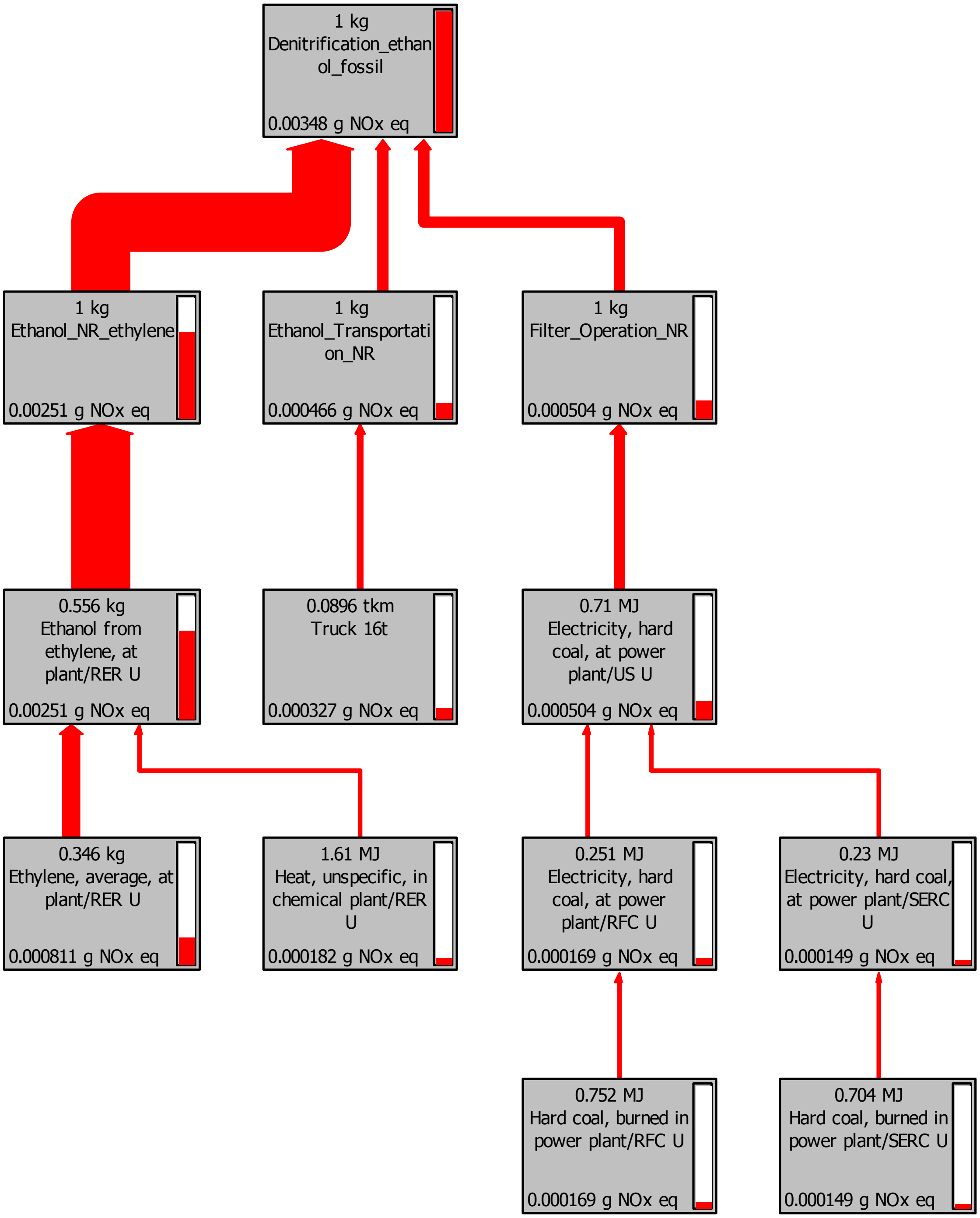

Figure A-36. Process flow diagrams of ethanol from fossil for smog impacts

Appendix B

LCA Impacts of Ethanol Based on Source

The global warming impact of ethanol from corn is larger than the global warming impact of ethanol from fossil fuels (Figure B-1). The units here are kg of CO2e (carbon dioxide equivalents) per kg of NO3- removed. Carbon dioxide equivalents are a method of accounting for different greenhouse gases and normalizing them to a single unit.

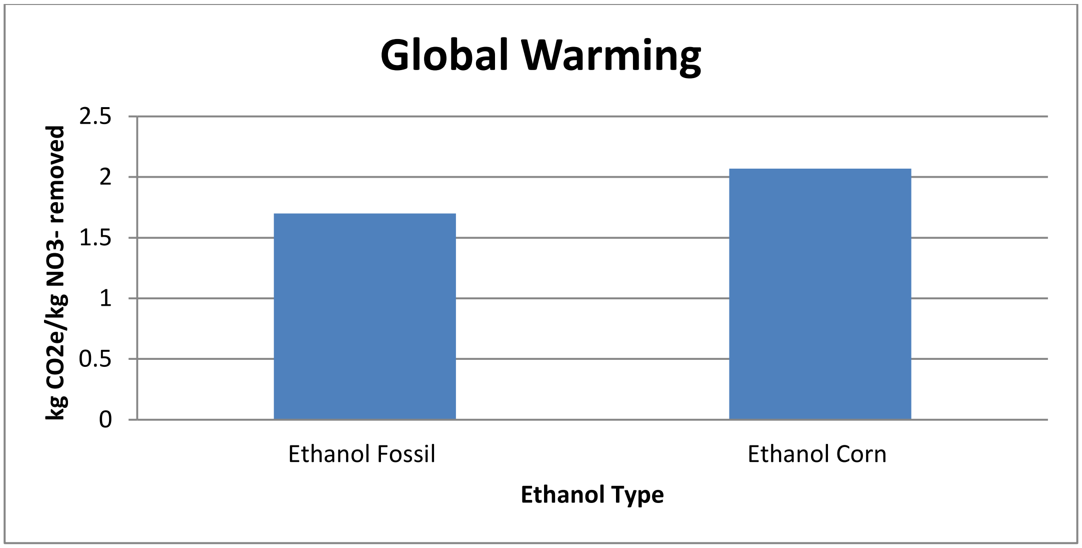

Figure B-1. Global warming impacts of ethanol produced from fossil and corn carbon sources

The acidification impact of ethanol from corn is greater than the impact of ethanol from fossil sources (Figure B-2). The units of acidification impact are expressed as H+ moles eq/ kg NO3- removed. This unit is in terms of the equivalent mass of the acid which can supply one mole of H+.

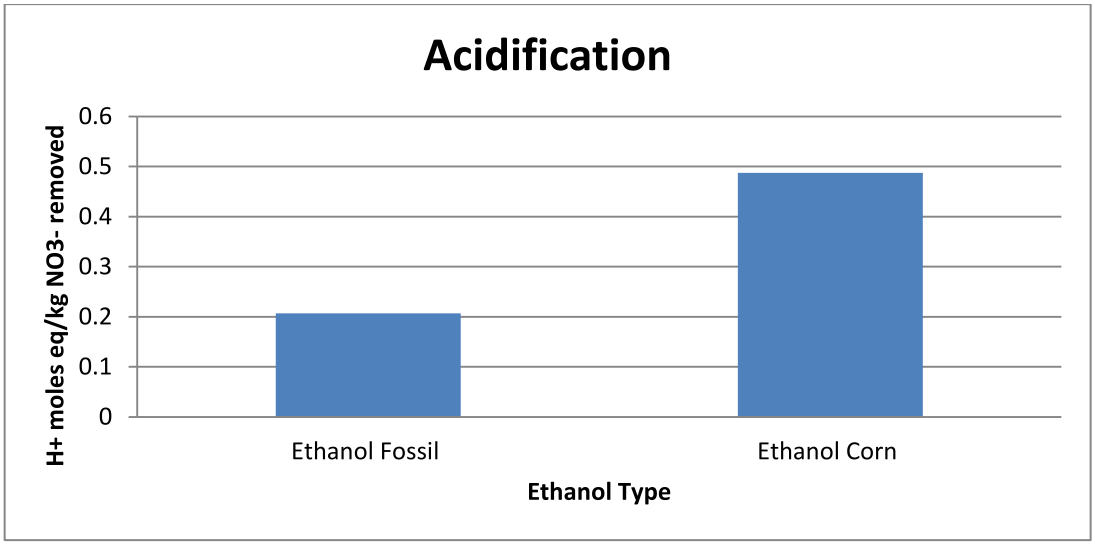

Figure B-2. Acidification impacts of ethanol produced from fossil and corn carbon sources

The carcinogenic impacts of ethanol from corn are greater than those of ethanol from fossil fuel (Figure B-3). The unit used here to express the impacts is kg of benzene (a carcinogen) equivalents. This unit conveys the number of kgs of benzene that would have to be emitted to pose the same health risks as the individual carcinogenic impacts.

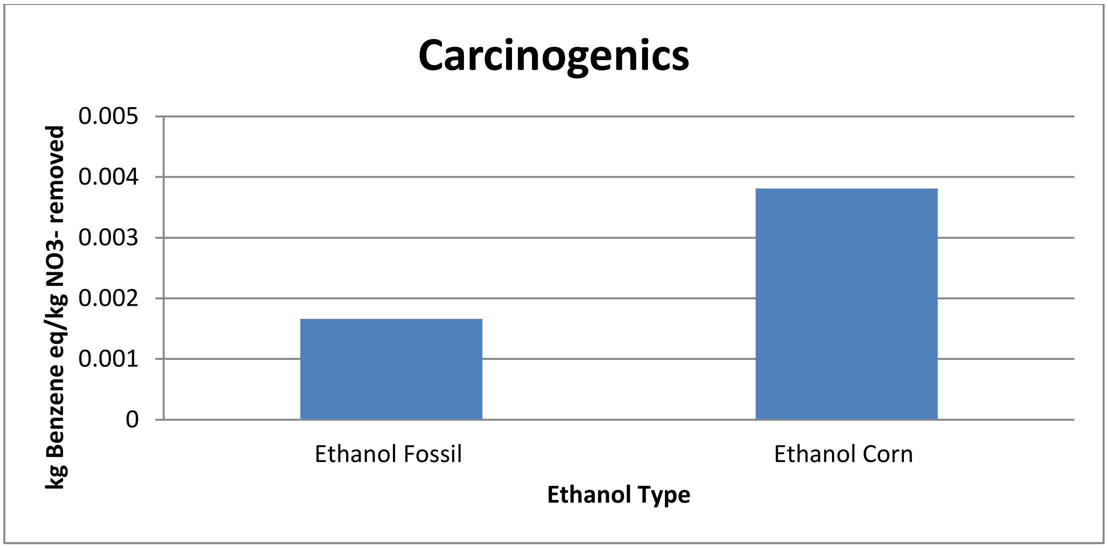

Figure B-3. Cacinogenics impacts of ethanol produced from fossil and corn carbon sources

The non-carcinogenic impact health of ethanol manufactured from corn is higher than that of ethanol manufactured from fossil sources (Figure B-4). The units in this case are expressed in terms of kg toluene equivalents. Toluene is a non-carcinogen, and this unit is utilized to normalize the effects of the various chemicals to the equivalent mass of toluene needed to produce the same level of impacts.

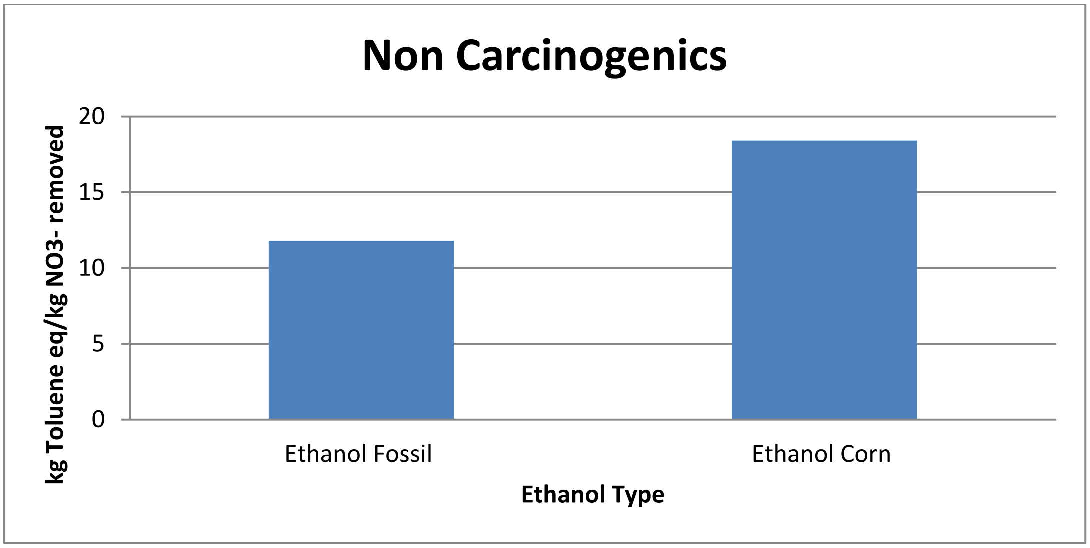

Figure B-4. Non-carcinogenics impacts of ethanol produced from fossil and corn carbon sources

Ethanol manufactured from corn has a larger respiratory impact than ethanol manufactured from fossil fuels (Figure B-5). The units for this measurement are in kg of PM2.5 eq, which is particulate matter with a diameter of 2.5 µm (microns) or less. Particles of this diameter and smaller have been linked to respiratory issues. This allows the respiratory impacts to be normalized on a basis of impact equivalent to PM2.5.

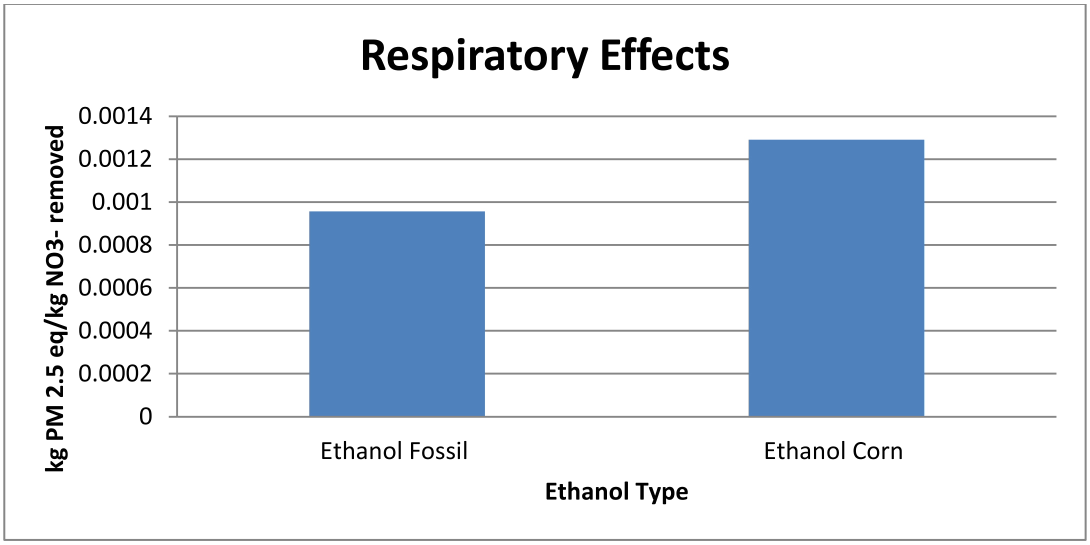

Figure B-5. Respiratory effects impacts of ethanol produced from fossil and corn carbon sources

Ethanol from corn was found to have a larger ozone depletion impact than ethanol from fossil fuels (Figure B-6). The units for this impact are kg CFC-11 (trichlorofluoromethane). CFC-11 is a compound that degrades the ozone layer. This unit term is utilized to normalize the ozone depletion impacts to the equivalent mass of CFC-11.

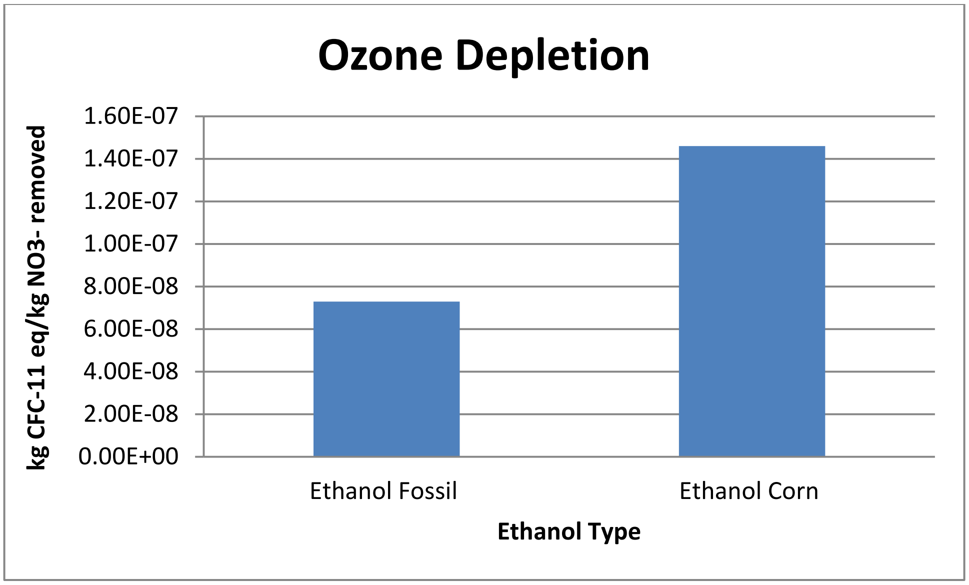

Figure B-6. Ozone depletion impacts of ethanol produced from fossil and corn carbon sources

Ethanol from corn has higher eutrophication impact than ethanol from fossil fuels (Figure B-7). These values are negative, meaning eutrophication impact avoided, thus the smaller of the negative values has the larger impact. The units are kg nitrogen eq, which is a unit based on eutrophication impact, which allows for the normalization to the impact that a kg of nitrogen would have.

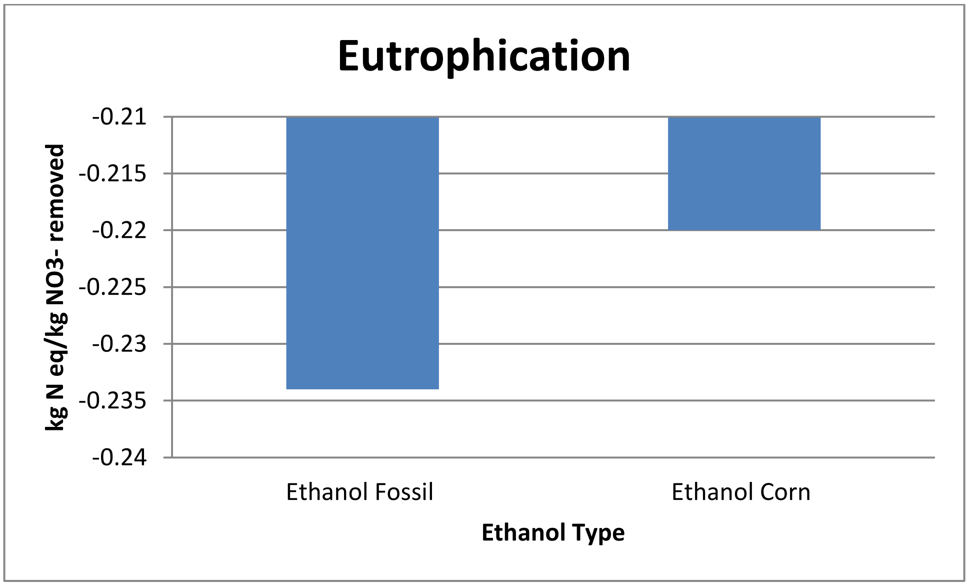

Figure B-7. Eutrophication impacts of ethanol produced from fossil and corn carbon sources

The ecotoxicity impact of ethanol from fossil sources is greater than the ecotoxicity impact of ethanol from corn (Figure B-8). This impact is measured in units of 2,4-D eq (2,4-

dicholorophenoxyacetic acid), an herbicide. The equivalency measure allows the ecotoxicity impacts of the different ethanol production processes to be normalized into one unit of impact equivalent to 2,4-D.

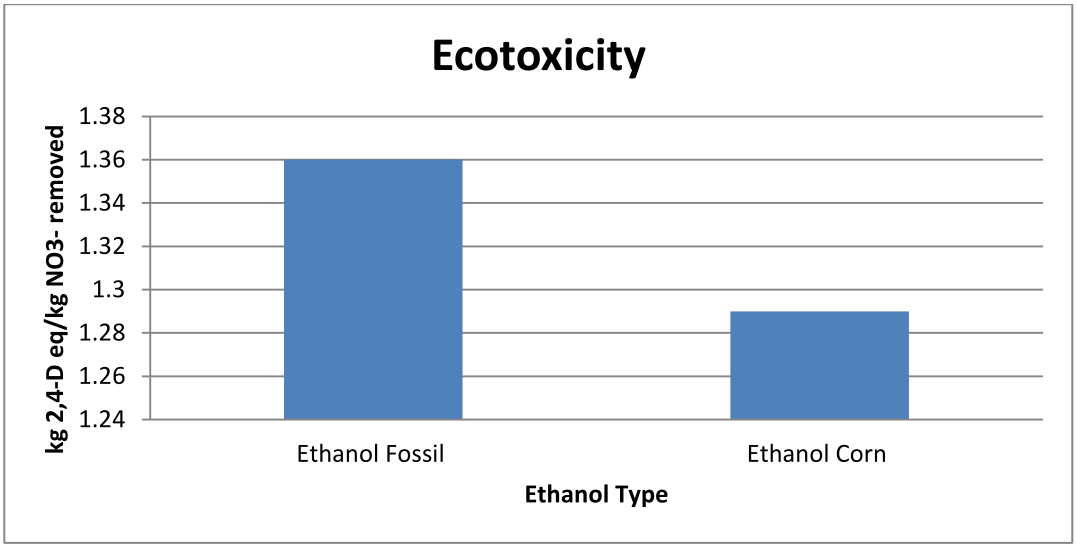

Figure B-8. Ecotoxicity impacts of ethanol produced from fossil and corn carbon sources

Ethanol production from fossil fuels has a larger smog impact than ethanol production from corn (Figure B-9). The units used to express this are g NOx eq, which is grams of NO (nitrogen oxide) and NO2 (nitrogen dioxide), generated during fossil fuel combustion that cause photochemical smog. This unit is used in order to normalize the impacts of the emissions to an equivalent impact from a mass of NOx.

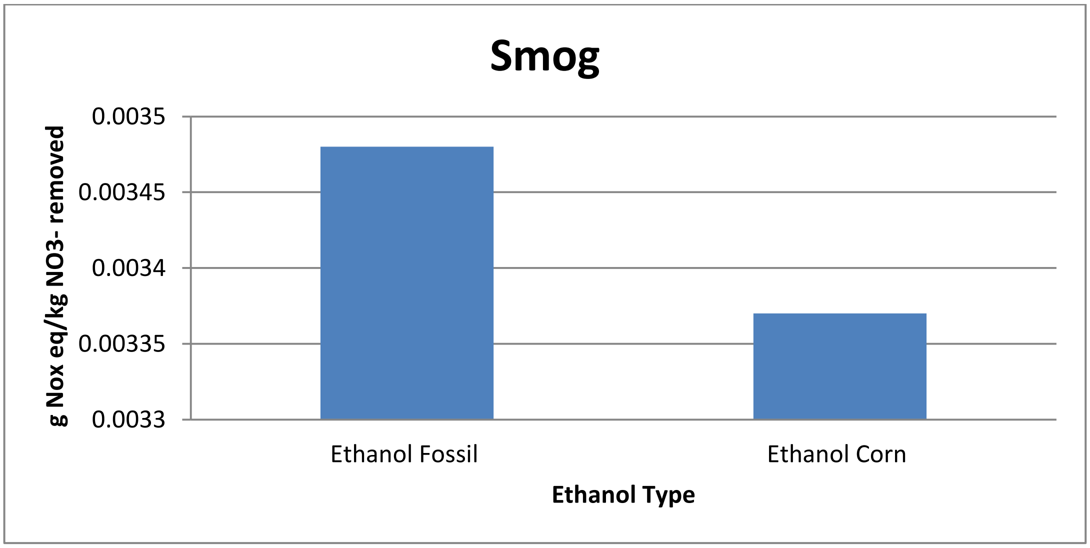

Figure B-9. Smog impacts of ethanol produced from fossil and corn carbon sources

Appendix C

LCA Impacts of Three Carbon Sources

The global warming impact of acetic acid is greater than that of the global warming impact of ethanol or methanol (Figure C-1). Methanol, of the three carbon sources evaluated, has the lowest global warming impact. The units here are kg of CO_2e (carbon dioxide equivalents) per kg of NO_3^- removed. Carbon dioxide equivalents are a method of accounting for different greenhouse gases and normalizing them to a single unit.

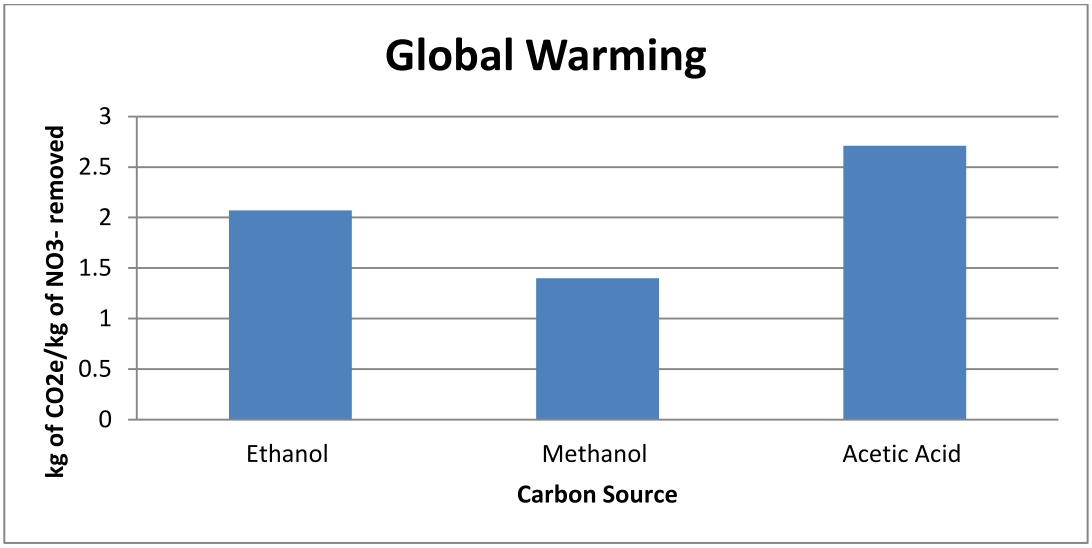

Figure C-1. Comparison of global warming impacts among the three external carbon sources

The acidification impact of ethanol is greater than the acidification impact of acetic acid and methanol (Figure C-2). Methanol has the lowest acidification impact of the three carbon sources studied. The units of acidification impact are H+ moles eq/ kg NO_3- removed. This unit is in terms of the equivalent mass of the acid which can supply one mole of H^+.

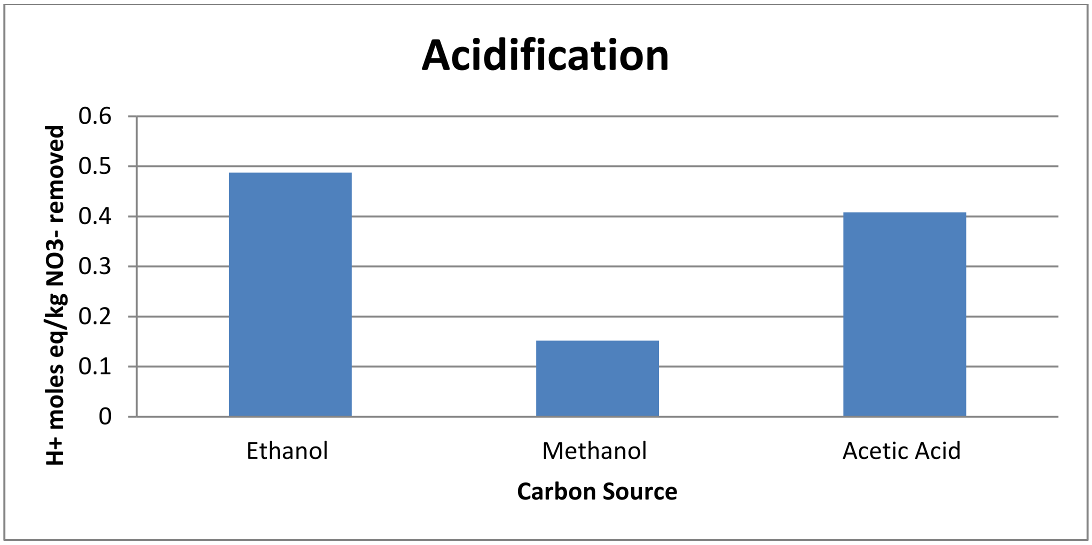

Figure C-2. Comparison of acidification impacts among the three external carbon sources

The carcinogenic impact of acetic acid is greater than the carcinogenic impact of ethanol and methanol (Figure C-3). Methanol has the lowest carcinogenic impact of the three external carbon sources studied. The unit is kg of benzene equivalents (a carcinogen). This unit represents the number of kgs of benzene that would have to be emitted to pose the same health risks as the individual carcinogenic impacts.

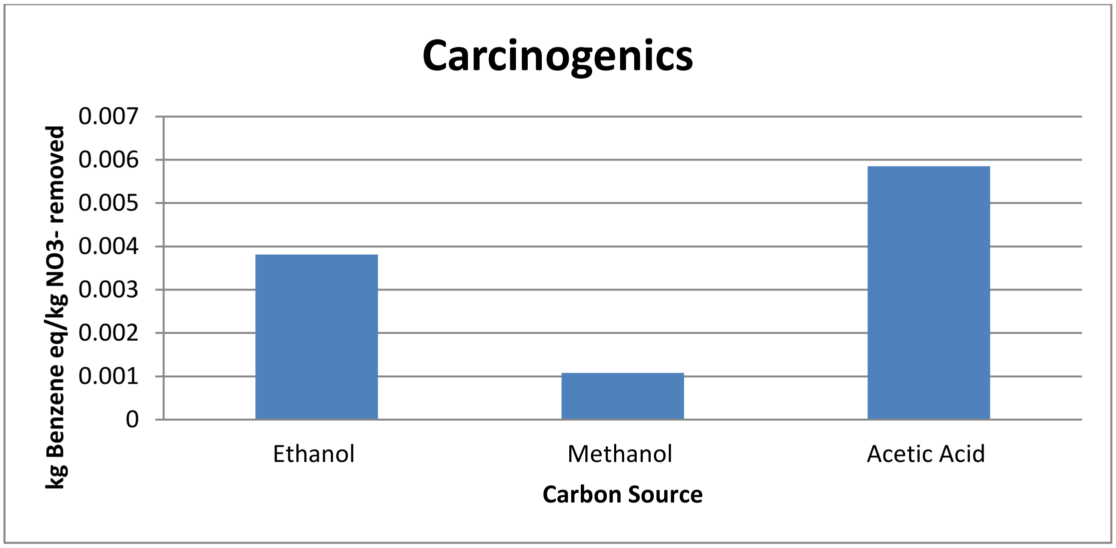

Figure C-3. Comparison of carcinogenic impacts among the three external carbon sources

The non-carcinogenic health impact of acetic acid is higher than the non-carcinogenic impact of ethanol and methanol (Figure B-4). Methanol has the lowest non carcinogenic impact of the three external carbon sources studied. The units in this case are expressed in terms of kg toluene equivalents. Toluene, a non-carcinogen, is used to normalize the effects of the various chemicals to the equivalent mass of toluene needed to produce the same level of impact.

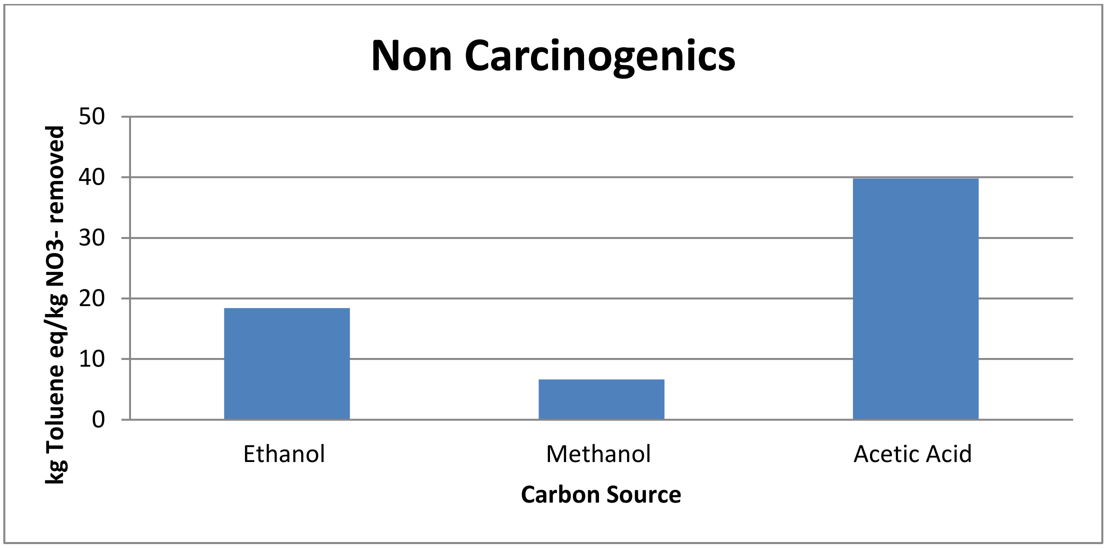

Figure C-4. Comparison of non carcinogenic impacts among the three external carbon sources

The respiratory effects of acetic acid are larger than the respiratory effects impact of ethanol and methanol (Figure B-5). Methanol was found to have the lowest respiratory effects of the three carbon sources studied. The units for this measurement are in kg of $PM_{2.5}$ eq, which is particulate matter with a diameter of 2.5 µm (microns) or less. Particles of this diameter and smaller have been linked to respiratory issues. This allows the respiratory impacts to be normalized on a basis of impact equivalent to $PM_{2.5}$.

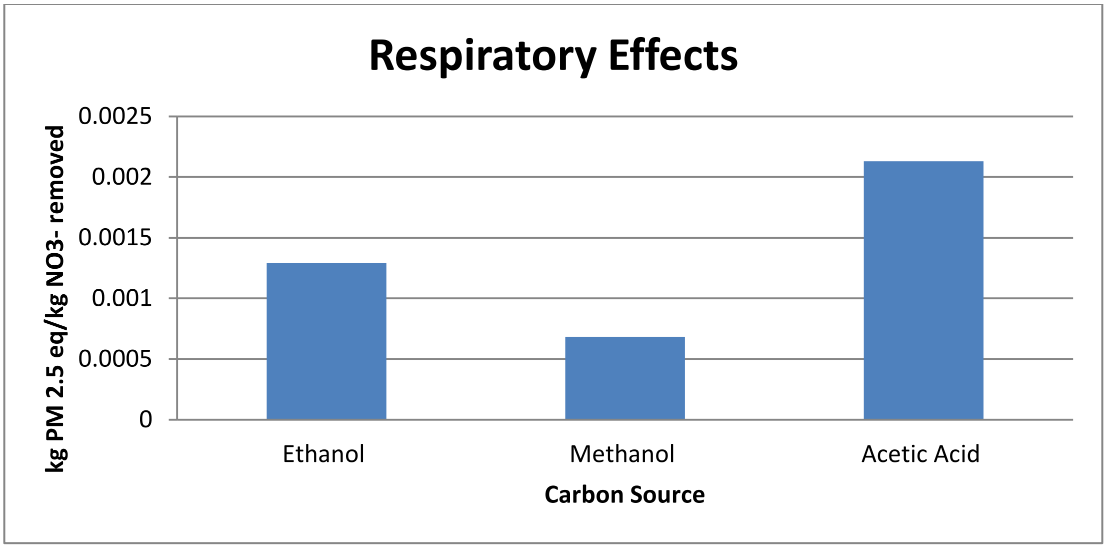

Figure C-5. Comparison of respiratory effects impacts among three external carbon sources

Ethanol has a larger eutrophication impact than methanol and acetic acid (Figure C-5) while methanol has the lowest smallest eutrophication impact of the three carbon sources studied. NO_3^- has a large eutrophication impact, and due to its avoidances, the eutrophication impact values are negative. Thus, the smaller of the negative values has the larger impact. The units utilized here are kg nitrogen eq, which is a unit based on eutrophication impact, which allows for normalization to the equivalent impact that a kg of nitrogen would have.

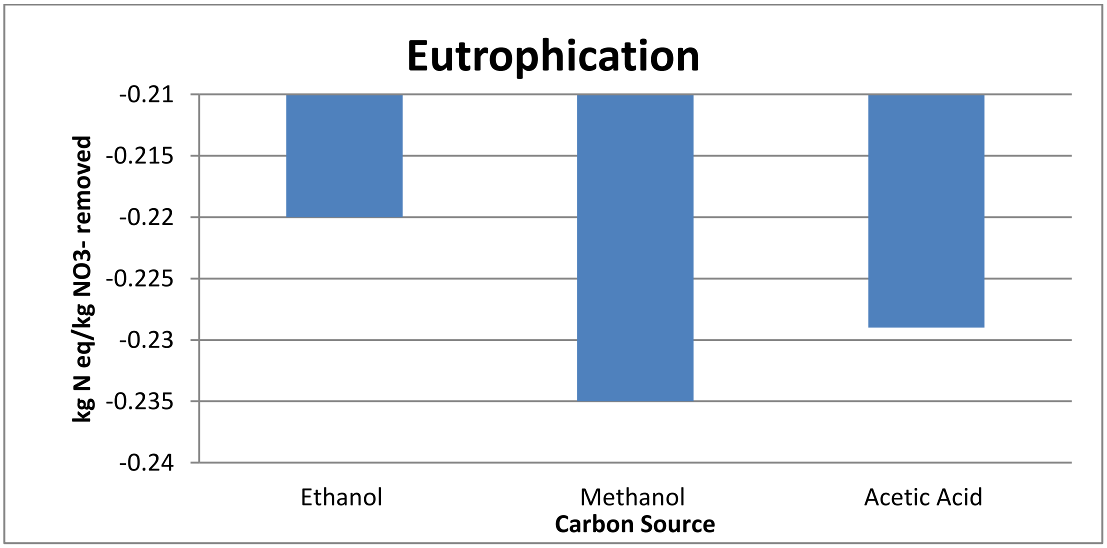

Figure C-6. Comparison of eutrophication impacts avoided among the three external carbon sources

The ozone depletion impact of acetic acid is larger than the ozone depletion impact of ethanol or methanol (Figure C-7). Ethanol has the lowest ozone depletion impact of the three carbon sources studied. Units for this impact are kg CFC-11 (trichlorofluoromethane). CFC-11 is a compound that degrades the ozone layer. This unit term is utilized to normalize the ozone depletion impacts to the equivalent mass of CFC-11.

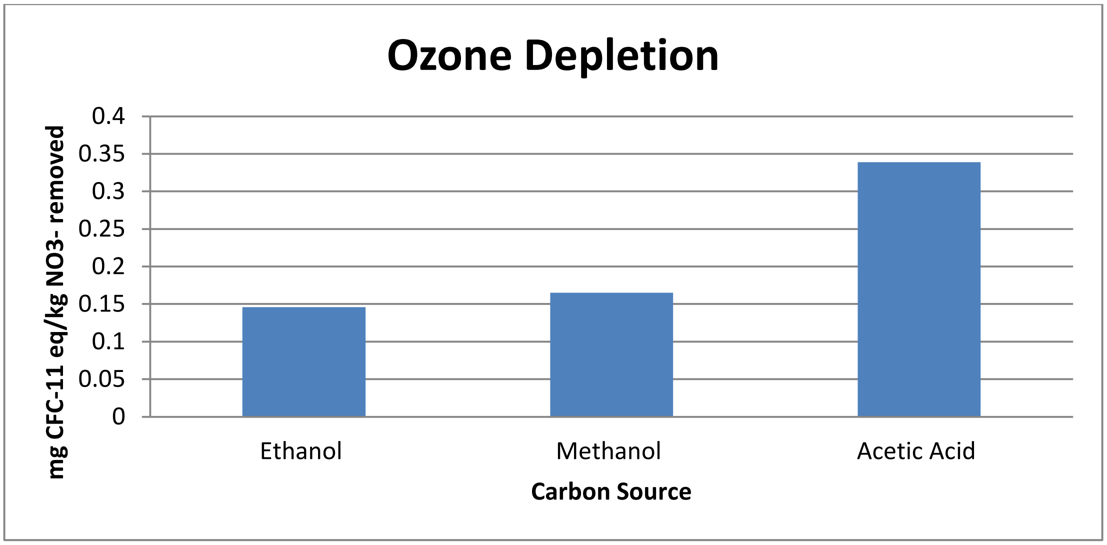

Figure C-7. Comparison of ozone depletion impacts among the three external carbon sources

The ecotoxicity impact acetic acid is larger than the ecotoxicity impacts of ethanol and methanol (Figure C-8). Methanol has the lowest ecotoxicity impact of the three carbon sources studied. This impact is measured in units of 2,4-D eq (dicholorophenoxyacetic acid), a pesticide and herbicide. The equivalency measure allows the ecotoxicity impacts of the different ethanol product processes to be normalized into one unit of impact equivalent to 2,4-D.

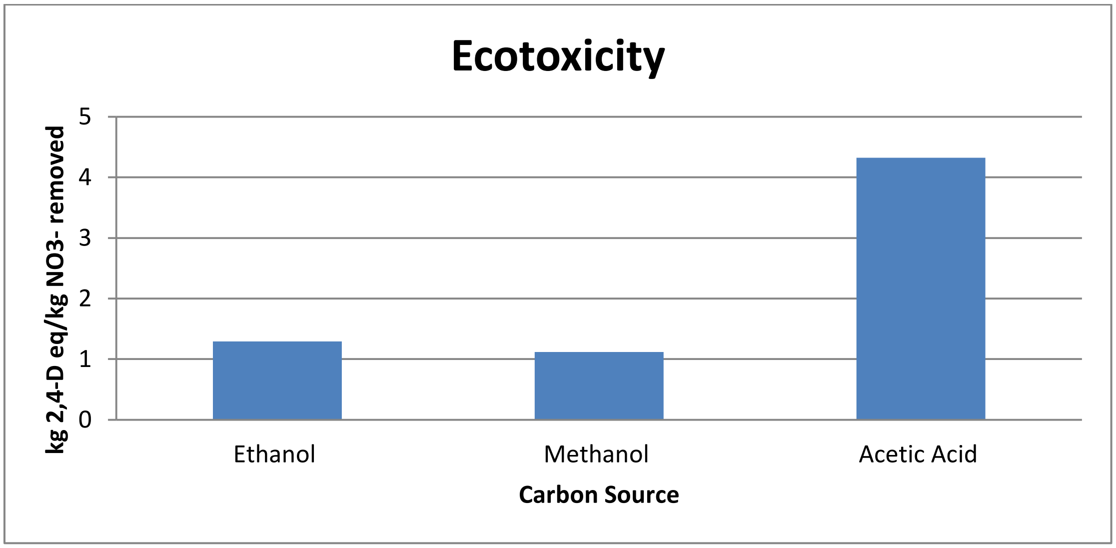

Figure C-8. Comparison of ecotoxicity impacts among the three external carbon sources

The smog impact is largest for acetic acid when compared to the smog impact for ethanol and methanol (Figure C-9). Methanol was found to have the lowest smog impact of the three carbon sources studied. The units used to express this are g NOx eq, which is grams of NO (nitrogen oxide) and NO_2 (nitrogen dioxide), which are nitrogen compounds generated during fossil fuel combustion that cause photochemical smog. This unit is utilized to normalize the impacts of the emissions to an equivalent impact from a mass of NOx.

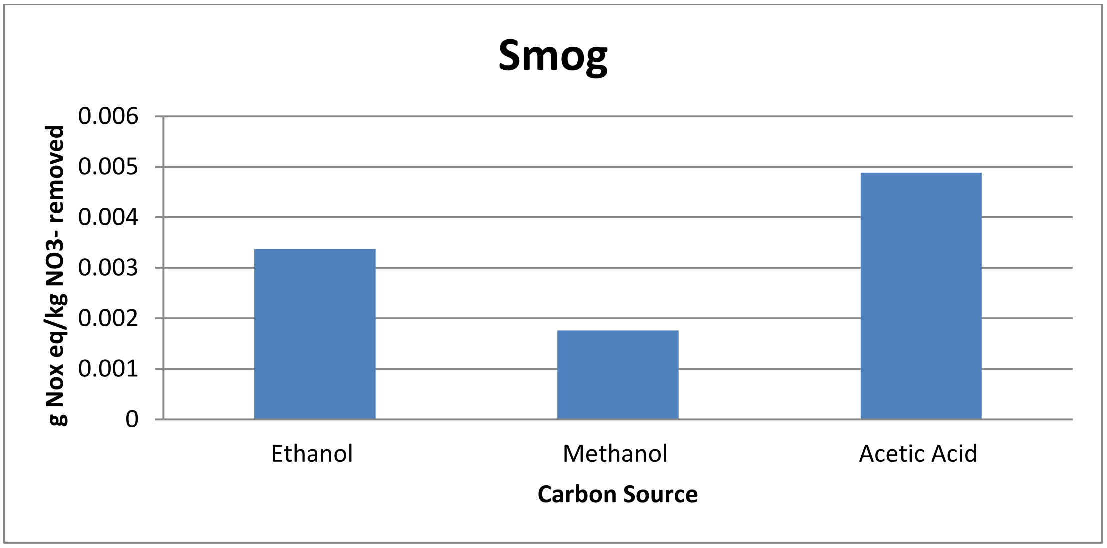

Figure C-9. Comparison of smog impacts among the three external carbon sources