SECTION I: REACTIVE NITROGEN

Reactive nitrogen can negatively affect human health and environmental health. This section provides a general perspective on reactive nitrogen, its relation to anthropogenic activities, especially agricultural practices, and examines the status of reactive nitrogen in Oregon.

Summary – Reactive nitrogen can negatively affect human health and environmental health. For the purposes of this report the term reactive nitrogen refers to only two compounds (1) nitrate anions (NO_3), and (2) nitrous oxide gas (N_2O) . These two species have well-documented links to human health and environmental health and are generated directly from agricultural fertilization practices through the complex, biological nitrogen transformation pathways found in soils and freshwaters. Although Earth's terrestrial biosphere is submerged in an ocean of nitrogen gas, it is a lack of available nitrogen that often constrains primary production in terrestrial and marine ecosystems and agro-ecosystems. This is because nitrogen gas is highly unreactive and must be "fixed" before it can enter the biosphere. For the greater part of life's history on Earth, the incorporation of nitrogen into biological molecules has occurred through enzyme-mediated nitrogen fixation. Nitrogen fixation $(N_2 \to NH_4^+)$, nitrification ($NH_4^+ \to NO_3^-$), and denitrification ($NO_3^- \to N_2$) constitute the main legs of the Earth's nitrogen cycle. Human activities began to dramatically affect the global nitrogen cycle starting in 1931 with the industrial production of $\mathrm{NH_4}^+$ from atmospheric N_2 using the Haber-Bosch process. Since 1931 outputs from the Haber-Bosch process have grown rapidly to the point that anthropogenic inputs now provide about 45% of the total fixed nitrogen produced annually on Earth. The global nitrogen cycle is a complex system of feedbacks and delays with behavioral characteristics that are still unknown and are most likely to be unanticipated and cascading. The recommended planetary boundary for the yearly amount of nitrogen fixed for human use is 35 Tg N yr⁻¹. Currently, we fix around 125 Tg N yr⁻¹ or more than 3.5 times the recommended boundary level. About 75% of anthropogenic nitrogen is used for synthetic fertilizer production.

Synthetic nitrogen fertilizers have been a boon to agricultural production and are responsible, in large part, for our ability to feed an exponentially growing human population. However, current agricultural practices are highly inefficient in their use of synthetic nitrogen fertilizers. Roughly, crop use efficiency for applied synthetic nitrogen fertilizers is at best around 50%. This means that a tremendous amount of reactive nitrogen enters the environment as either nitrate or nitrous oxide: nitrate is completely water soluble and can contaminate freshwaters and ocean waters; nitrous oxide gas enters the atmosphere as a greenhouse gas that is 300x more potent than carbon dioxide. Nitrate contamination of groundwater is a serious issue in Oregon. Oregon ranks among the top 10 states identified as having the highest nitrate concentrations in shallow groundwater in the United States and nitrate is the most commonly detected contaminant in Oregon's groundwater, followed by pesticides, volatile organic compounds, and bacteria. Between 1987 and 2006 Oregon used an average of about 150,000 tons of nitrogen per year from synthetic nitrogen fertilizers. Over the past 20 vears the State has conducted limited, comprehensive ambient groundwater quality studies on nitrate contamination. These data were responsible for the designation of three, Groundwater Management Areas (GWMAs) in the state where nitrate contamination was believed to be consistently at or above 7 ppm (mg NO_3/L). The federal drinking water standard for nitrate is 10 ppm. Although there are currently no state or federal greenhouse gas emissions regulatory levels, DEO estimates that the mean total of greenhouse emissions for a recent 20-year period (1990 – 2010) in Oregon was about 65,800 Gg CO₂eq. Most of the greenhouse gas emissions from agricultural activities in the state are in the form of methane and nitrous oxide, not carbon dioxide. DEQ estimates that the mean total emissions from agricultural activities for the same 20-year period (1990 - 2010) were 5,500 Gg CO₂eq or about 8.4% to the State's total greenhouse emissions.

Reactive Nitrogen

This subsection defines reactive nitrogen and briefly explains important aspects of the global nitrogen cycle.

Definition of Reactive Nitrogen (Nr)

Reactive nitrogen (Nr) is a term that, in its broadest sense, refers to any nitrogen-containing molecule with a non-zero oxidation state; that is, any nitrogenous compound except for nitrogen gas or diatomic N_2 . More typically the term refers to a small class of nitrogen-based compounds that are specifically defined by a community of practice. For example, the atmospheric chemistry community often defines reactive nitrogen as any N-O combination except N_2O (e.g., NOx, N_2O_5 , HNO_2 , HNO_3 , nitrates, organic nitrates, halogen nitrates, etc). A much broader definition is used by Galloway et al. (2004) as "all biologically active, photochemically reactive, and radiatively active N compounds in the atmosphere and biosphere of the Earth ... [and] includes inorganic reduced forms of N (e.g., NH_3 , NH_4), inorganic oxidized forms (e.g., NOx, HNO_3 , N_2O , NO_3), and organic compounds (e.g., urea, amines, proteins, nucleic acids)."

For the purposes of this report the term reactive nitrogen will refer to only two compounds (1) nitrate anions (NO_3) , and (2) nitrous oxide gas (N_2O) . This is because these two species have well-documented links to human health and environmental health and are generated directly from agricultural fertilization practices through the complex, biological nitrogen transformation pathways found in soils and freshwaters. (UNEP and WHRC, 2007; Galloway et al., 2004: Canfield et al., 2010).

Important Nr Pathways in the Nitrogen Cycle

Earth's terrestrial biosphere is submerged in an ocean of nitrogen gas. This atmospheric gas is commonly referred to as simply nitrogen although it is in fact N_2 . The troposphere, the lowest layer of Earth's atmosphere, is about 78% nitrogen gas (v/v) and appears to offer a near limitless supply of elemental nitrogen for the synthesis of two of life's most critical polymers, nucleic acids and proteins. It is worth noting that life's requirements for elemental nitrogen are enormous with living systems typically maintaining about a 10-to-1 C:N ratio in their cells (Canfield et al., 2010). It is also noteworthy that because of its eight oxidation states, the numerous mechanisms for interspecies conversion, and a variety of environmental transport and storage processes, nitrogen has perhaps the most complex cycle of all the major elements (Galloway et al. 2004). Surprisingly, it is a lack of available nitrogen that often constrains primary production in terrestrial and marine ecosystems. This is true in agro-ecosystems as well. In these cases elemental nitrogen actually becomes a limiting plant nutrient. How is this possible with so much atmospheric nitrogen available? The answer lies in the chemical nature of N_2 . Atmospheric nitrogen is inert or chemically unreactive and so does not, by itself, enter into biochemical reactions. The triple bond between the two atoms of nitrogen in N_2 is incredibly strong (about 950 kJ/mol) and must be broken before nitrogen is made available ('fixed') for biological use.

For the greater part of life's history on Earth and except for some atmospheric nitrogen fixed by lightning, the incorporation of nitrogen into biological molecules has occurred through enzyme-mediated nitrogen fixation. Nitrogen fixation, then, is the first important major pathway in the nitrogen cycle. *Nitrogen fixation* is the process whereby prokaryotes in the bacterial and archaeal domains reduce atmospheric N_2 to ammonium (NH_4^+) with the help of the nitrogenase enzyme complexes. Globally, the natural rate of terrestrial nitrogen-fixation is about 8×10^{12} mol yr⁻¹ (Canfield et al., 2010).

Although ammonium is rapidly assimilated into the biosphere, there are other soil microbial processes that very rapidly oxidize the ammonium cation NH_4^+ to the nitrate anion NO_3^- . This enzyme-mediated process is known as *nitrification* and is the second important major pathway in the nitrogen cycle. Nitrification produces significant amounts of nitrous oxide (N_2O) gas in addition to the nitrate anion. Nitrification is thus the principal pathway for the production of reactive nitrogen, Nr in the environment. The process of nitrification is directly related to oxygen availability and the concentration of NH_4^+ in the soil. Interestingly, the electrons and protons

derived in this part of the nitrogen cycle are used by chemoautotrophic microbes to fix inorganic carbon in the absence of light (Canfield et al., 2010). That is, these microbes use the ammonium as an energy source and not as a nitrogen source.

The last leg of the nitrogen-cycle is *denitrification* which reduces NO_3 back to N_2 gas. Again, the chemical transformations are enzymatically complex and are performed through a variety of microbial communities. Significant amounts of N_2O are produced in this leg of the cycle as well.

Reactive Nitrogen and its Relationship to Agricultural Practices

This subsection discusses important impacts of human activities to the global nitrogen cycle, defines the term synthetic fertilizer, and discusses the role of modern agriculture in generating reactive nitrogen.

Anthropogenic Inputs to the Nitrogen Cycle

The biosphere requires vast amounts of nitrogen to build the molecules of life. As noted above, this nitrogen is all taken directly from the nitrogen gas which constitutes about 78% of the atmosphere. Fixed nitrogen in the recent and geologic past was a limiting nutrient for primary production because of the relatively limited quantities of NH₄⁺ produced by biotic N-fixation. Abiotic N-fixation by geophysical processes contributes very little to the global total. Human activities began to dramatically affect the global nitrogen cycle beginning in the early part of the 20th century. In 1931 the first industrial production of NH₄+ from atmospheric N₂ (using the Haber-Bosch process) went on-line in Germany. Of note is that the Haber-Bosch process currently is entirely dependent on methane (a petroleum resource) for its source of hydrogen gas and requires massive energy inputs to maintain favorable reaction conditions (between 400 - 450 °C and around 200 atm). In 2008, the global production of NH⁴⁺ using the Haber-Bosch process was approximately 9.5 x 10¹² mol NH₄+(Canfield et al., 2010), of which about 75% was used for synthetic fertilizer production. The quantity of N-fixation cultivation also has been growing and has increased to an annual production of about 2.4 x 10¹² mol N. Finally, the 20th century has seen a dramatic rise in fossil fuel combustion which contributes yet another 2 x 10¹² mol NH₄⁺ to the annual global pool. Taken collectively, anthropogenic inputs now provide about 45% of the total fixed nitrogen produced annually on Earth. Perhaps of more concern is that the *rate* of anthropogenic production is currently double that of natural terrestrial production (Canfield et al., 2010).

Synthetic Fertilizers

A synthetic fertilizer is very generally a fertilizer produced by chemical mixing during manufacturing (Cornell University, 2014). A more extended definition is that a synthetic fertilizer is a substance formulated or manufactured by a chemical process or by a process that chemically changes a substance extracted from naturally occurring plant, animal, or mineral sources and that contains a single or blended substance that has one or more recognized plant nutrient(s) and which is used primarily for its plant nutrient content (National Organic Program, 2000). Synthetic fertilizers most often are formulated to deliver the major plant nutrients nitrogen (N), phosphorous, (P), and potassium (K). In the context of this report, synthetic nitrogen fertilizers are defined as those that contain some form of plant-available nitrogen where the original source of the fixed nitrogen was produced by the Haber-Bosch process. Plant-available nitrogen means either of the two chemical forms of fixed nitrogen that are actually available to plants; namely, NH₄⁺ or NO₃. For example, solid synthetic nitrogen fertilizers typically contain urea, (CO(NH₂)₂), which is produced by reacting ammonia gas (NH₃) with carbon dioxide (CO₂). Urea is completely water soluble and once applied to cropland it is rapidly hydrolyzed to gaseous ammonia. This often leads to undesirable losses of fixed nitrogen before soil organisms can reduce the ammonia gas to NH₄⁺ or oxidize it to NO₃ (International Plant Nutrition Institute, 2014). Of note is that prior to synthetic nitrogen fertilizers, cultivating legumes, recycling animal manure and crop residues, and mining ancient and contemporary deposits of bird and bat droppings were the primary sources of nitrogen in agriculture.

Agriculture and Reactive Nitrogen

Synthetic nitrogen fertilizers have been a boon to agricultural production and are responsible, in large part, for the success of the Green Revolution and our ability to feed an exponentially growing human population. There is absolutely no question that we will continue to depend on massive amounts fixed nitrogen for food production and that, in fact, our need for fixed nitrogen will most likely increase. For example, from 1960 to 2000 the world-wide use of nitrogen fertilizer increased about 800% with wheat, rice, and maize accounting for about 50% of the current use (Canfield et al.. 2010). However, current agricultural practices are highly inefficient in their use of synthetic nitrogen fertilizers. As noted above, agroecosystems receive about three-quarters of the world's fixed nitrogen as produced by the Haber-Bosch process. Roughly, crop use efficiency for applied synthetic nitrogen fertilizers is at best around 50%. For wheat, rice, and maize the nitrogen use efficiency is typically below 40% (Canfield et al.. 2010). This means that only about one-half of all applied synthetic nitrogen fertilizer is assimilated into biomass. Most of the fixed nitrogen that remains after plant uptake is either lost back to the atmosphere (about 25%) or leached out of the crop root zone and discharged to aquatic systems (about 20%). A very small amount of applied fixed nitrogen is actually retained by the agroecosystem in the soil (about 5%) (Galloway et al. 2004; Canfield et al. 2010).

Here lies the fundamental quandary. We must grow food but our current agricultural practices are the primary source of anthropogenic reactive nitrogen at global scales. For example, nitrate is now one of the most widespread contaminants in aquifers around the world and current agricultural practices account for about one-quarter of global nitrous oxide emissions. The deleterious effects of reactive nitrogen on human and environmental health are discussed in detail Section II and Section III of this report. Perhaps of even greater concern is that, with regards to nitrogen fixation, we have already substantially transgressed a so-called, 'planetary boundary.' In 2009 Johan Rockström and colleagues extended the 'footprint' idea of human impact to define nine planetary boundaries or control variables that collectively "define the safe operating space for humanity with respect to the Earth system and are associated with the planet's biophysical subsystems or processes" (Rockström et al. 2009). In quantifying these planetary boundaries Rockström and his numerous colleagues took "a conservative, risk-averse approach" knowing that, in general, Earth's complex systems often have dramatic, nonlinear responses to smooth, incrementally changing inputs. That is, many complex systems have key variables that are extremely sensitive around a threshold value. In such a system, crossing a threshold value often shifts the entire system into a completely new state, similar to a phase change in a purely physical system (Seydel, R. 2010). In the context of major subsystems of Earth such state changes could well have potentially disastrous consequences for humans. The reality is that the global nitrogen cycle is a complex system of feedbacks and delays with behavioral characteristics that are still unknown and are most likely to be unanticipated and cascading. The recommended planetary boundary for the yearly amount of nitrogen fixed for human use is 35 Tg N yr⁻¹. Note that Tg means 'teragram' and is equal to one trillion grams. Currently, we fixed around 125 Tg N yr⁻¹ or more than 3.5 times the recommended boundary level.

Reactive Nitrogen in Oregon

This subsection discusses the status of reactive nitrogen in groundwater and as atmospheric emissions in Oregon as of mid-2014.

Nitrate Inventories in Groundwater

Groundwater is a vital component of Oregon's natural resources and makes up about 95 % of the State's total available freshwater resources (DEQ, 2011a). Groundwater exists, at various depths, virtually everywhere beneath the land surface in Oregon and has a direct connection to surface waters as a major source of water for many of the state's springs, streams, lakes, and wetlands. Streams, for example, gain inflow directly from groundwater via springs and seepage into the streambed, especially during the late summer months. This water exchange between groundwater and streams provides the cool water that is so important for fish spawning. The reverse process, where streams lose water to groundwater, also occurs and can be a mechanism for aquifer

recharging (OWRD, 2012). Groundwater also is the primary source of drinking water in the State: approximately 70 % of all Oregonians rely solely or in part on groundwater for their drinking water. This figures jumps to over 90% for rural Oregonians. Currently, there are over 350,000 individual private domestic wells in the state. In recognition of the importance of groundwater as a vital natural resource, the State Legislature enacted the Oregon Groundwater Protection Act in 1989. The expressed goal of the Groundwater Protection Act is "to prevent contamination of Oregon's ground water resource while striving to conserve and restore this resource and to maintain the high quality of Oregon's ground water resource for present and future uses" (ORS 468B.155, 2013). The Department of Environmental Quality is tasked with the primary responsibility for implementing groundwater protection in Oregon and uses a combination of water quality and land use programs to implement the Act (OWRD, 2012).

Nitrate contamination of groundwater is a serious issue in Oregon. Oregon ranks among the top 10 states identified as having the highest nitrate concentrations in shallow groundwater in the United States and nitrate is the most commonly detected contaminant in Oregon's groundwater, followed by pesticides, volatile organic compounds, and bacteria (OWRD, 2012). Freshwaters naturally have some background concentration of nitrate, typically below 2-3 parts per million (ppm; as mg NO₃/L). But a variety of human health and environmental health problem arise at concentrations above 5 ppm nitrate (see Section II and Section III of this report.) Note that the maximum contaminant level (MCL) for nitrate in drinking water is 10 ppm which is an enforceable regulation as set by the EPA under the Safe Drinking Water Act (EPA, 2014a). Nitrate contamination of groundwater can come from numerous sources predominantly synthetic nitrogen fertilizers (particularly when used in irrigated agriculture), on-site (septic) systems for human waste, effluent from sewage treatment, livestock wastes, wastewater from food processing, and urban stormwater (DEQ, 2001b). Between 1987 and 2006 Oregon used an average of about 150,000 tons of nitrogen per year from synthetic nitrogen fertilizers for farm use peaking in 2003 and 2004 at about 200,000 tons (USGS, 2012). For comparison, during the same period California used an average of about 570,000 tons of nitrogen per year and Washington used an average of 200,000 tons of nitrogen per year. Based on these data and given the total land area per state (Oregon = 255,026km²; California = 423,970 km²; Washington = 184,827 km²), Oregon applies roughly about 0.6 tons N/km² as compared to California which applies roughly about 1.3 tons N/km² and Washington which applies roughly about 1.1 tons N/km². Note that these data exclude nitrogen contributions from urban areas (i.e., lawn fertilization). Not surprisingly, nitrate contamination of groundwater is a regional as well as a national problem and tends to be directly related to synthetic nitrogen fertilizer inputs (DEO, 2011b).

Over the past 20 years the State has conducted limited, comprehensive ambient groundwater quality studies and continues to collect a limited amount of data on nitrate contamination. Between 1980 and 2000 DEQ conducted 45 groundwater quality assessments which covered only 6.4 percent of the total land area of the state, but 30.8 percent of the area in Oregon where groundwater is used. The results of these assessments indicated that 35 of 45 study areas showed some impairment or reason for concern with nitrate contamination being the dominant reason for concern. Oregon law now requires well water testing when real-estate property is sold if the well is used as a source of drinking water. Well water samples collected during home sales (so-called real-estate transaction data) show several areas in the state where nitrate levels are above safe levels in private domestic wells. In 2004, DEQ obtained a grant from the EPA to create a database and summarize the real-estate transaction data. These data provide a broad overview of groundwater quality across the state, as well as some observations about nitrate levels in specific locations. Currently, these data show that, based on the implemented sampling and analysis protocols, most domestic drinking water wells (82%) have nitrate levels at or below 2 ppm reflecting background groundwater quality. Approximately 14 % of the test results showed nitrate levels above background groundwater quality and about 2% of the wells tested exceeded the federal drinking water standard of 10 ppm (OWRD, 2012). The wells showing greater than background levels of nitrate are not randomly distributed across the state but are in fact concentrated in three specific areas (see below). Additionally, 21 Oregon public water systems reported federal violations of the MCL for nitrate in 2010 while 66 public water systems had nitrate concentrations equal to or greater than half the MCL (DEQ, 2011b). Finally, a recent DEQ report indicates that there are seventy community and non-transient non-community public water supplies in Oregon that met the report's screening criteria for having current nitrate problems or being at risk of developing nitrate problems (DEQ, 2011b). Additionally, the report identified many more transient non-community public water systems and state regulated non-public systems that met the screening criteria but were not analyzed because of limited public consumption of water from these sources. The smaller public water systems that were identified in the report serve smaller populations such as mobile home parks or rural schools and the report raises "possible environmental justice concerns about socioeconomically vulnerable populations being exposed disproportionately."

In Oregon, the detection of contaminants in groundwater at one-half the drinking water standard, or at 70% of the nitrate drinking water standard of 10 ppm (i.e., 7 ppm) can be the basis for declaring a Groundwater Management Area (GWMA) and in fact, there are currently three GWMAs in the state covering portions of Linn, Lane, and Benton Counties, the Lower Umatilla Basin, and northern portions of Malheur County (DEQ, 2011a; OWRD, 2012)). The three GWMAs are identified as (1) the Southern Willamette Valley GWMA, (2) the Lower Umatilla Basin GWMA, and (3) the Northern Malheur County GWMA.

Southern Willamette Valley GWMA

Between 2000 and 2001 DEQ sampled 476 wells in Linn, Lane, and Benton counties and subsequently tested these samples for nitrate, pesticides, bacteria and a variety of other parameters. Over 20% of the sampled wells had nitrate concentrations in excess of 7 ppm with the highest level detected within the study area being 23 ppm. Approximately 89% of the wells sampled in the 2000 – 2001 study had values greater than 7 ppm were located in or relatively adjacent to the sand and gravel deposits associated with the Willamette River and its tributaries (DEQ, 2003). In 2002 re-sampling was done on those wells that had tested greater than 7 ppm in the original study. The 2002 study confirmed nitrate concentrations greater than 7 ppm with a maximum concentration of 28 ppm. In 2004 the DEQ declared a GWMA for portions of the Southern Willamette Valley covering an area of approximately 2020 km² (DEQ, 2011a). Since 2004 DEQ has continued to monitor groundwater nitrate concentration in the Southern Willamette GWMA. Monitoring efforts include 41 wells being regularly sampled and periodic 'synoptic events' that sample and test additional wells (in 2009, over additional 100 wells) to assess regional changes in groundwater nitrate concentrations. In 2008 a study was done to assess the relative contributions of nitrogen loading to the groundwater of the GWMA by major land use categories (LCOG, 2008). The model created by the study estimated a composite total nitrogen input to groundwater in the GWMA of about 1885 N yr⁻¹ with crops contributing 90%, confined animal feeding operations (CAFOs) contributing 6%, and septic systems contributing 4% of the total. The Action Plan for the Southern Willamette Valley GWMA, which was approved in 2006, provides 60 strategy recommendations keyed to the area's stakeholders to reduce nitrate contributions and prevent further groundwater contamination in the GWMA. DEQ analysis indicates that the area-wide nitrate trend in the GWMA was steady or slightly decreasing. (DEQ, 2011a).

Northern Malheur County GWMA

In 1985 DEQ sampled 107 wells in northern Malheur County and found that 34% of these had nitrate levels above 10 ppm. An additional concern was the presence of the pesticide Dacthal® (tetrachloroterephthalate) and its metabolites in the samples. The DEQ study pointed to the contamination of the groundwater in the region's shallow alluvial sand and gravel aquifer which receives a large proportion of its recharge from irrigation via infiltration of irrigation canal waters and direct seepage from irrigation water. Agriculture is the dominant land use category in the region (DEQ, 2011a). The Northern Malheur County GWMA was declared in 1989 and covers an area of about 465 km². The GWMA boundary starts at the mouths of the Malheur and Owyhee Rivers and extends to the uppermost irrigation canals. In 1991 an Action Plan was approved by the stakeholders of the GWMA action committee with recommendations for voluntary adoption of practices and activities that would

reduce contaminant loading to groundwater such as alternative irrigation and fertilization management practices. Success of the Action Plan is measured by the adoption of Best Management Practices (BMPs) and improvement in water quality within the GWMA. Groundwater quality assessment monitoring in this GWMA by DEQ has been on-going since 1989 and currently includes a network of approximately 35 wells that are tested every other month for nitrate and Dacthal® as well as a more complete analysis approximately once per year. In 2010 a formal trend analysis of nitrate concentrations was conducted with the 18 years of data collected since implementation of the GWMA action plan (1991 through 2009) (DEQ, 2010). The analysis indicated that the area-wide nitrate trend was slightly decreasing with individual wells either decreasing (58%), increasing (22%), or showing no statistically significant change (19%). As of 2011, DEQ notes that "progress is being made on the land surface through the implementation of BMPs. However, it may take years or even decades for groundwater quality to return to natural background levels" (DEQ, 2011a).

Lower Umatilla Basin GWMA

The DEQ established the Lower Umatilla Basin GWMA in 1990. This GWMA covers an area of 1424 km² in the northern portions of Umatilla and Morrow counties. Since 1991 DEQ has established a groundwater monitoring program that includes a network of about 31 wells which are regularly sampled for nitrate analysis. An additional 107 wells (the so-called synoptic well network) is sampled sporadically. The synoptic well network has been sampled three times; in 1992, 2003 and 2009 (GSI, 2013). As always, the goal of the DEQ monitoring program is to provide sufficient data to evaluate the distribution, sources, and trends of nitrate contamination in groundwater. In 1997 the GWMA action committee adopted an Action Plan that called for decreasing nitrate trends throughout most of the GWMA by the end of 2009. The 1997 Action Plan also identified and ranked the potential sources of nitrogen loading to groundwater in the GWMA into three tiers based on the estimated contribution of each tier to the total. Tier I, identified as irrigated agriculture, contributes an estimated 82% of the nitrogen loading to groundwater in the GWMA; Tier II, identified as pastures, food-processors, and septic systems, contributes an estimated 16% of the nitrogen; and Tier III, identified as lawns, manure spreading, vegetable gardens, and the Depot Washout Lagoon, contributes an estimated 2% (Richerson, 2011). In 2012 GSI Solutions, Inc., was awarded a \$50,000 Fertilizer Research Program Grant from the Oregon Department of Agriculture "to perform an independent review of DEQ's groundwater monitoring program "over a three-year period. The first report from GSI Solutions, Inc., (June 2013) makes specific recommendations for revised sampling and statistical analysis and suggests that DEQ re-run some of its data because "there are indications that implementation of BMPs described in the Action Plan are potentially having a positive impact on groundwater quality (e.g., more wells showing no trend or a decreasing nitrate trend) ' (GSI, 2013). The GSI Solutions, Inc., report comes on the heels of the third, four-year evaluation of the Lower Umatilla Basin GWMA Action Plan by DEQ. In this report DEQ notes "area-wide nitrate concentrations are high and trends continue to increase 15 years after adopting the plan. While the nitrate concentrations in our area continue to show increases, the rate of increases are less than in past years (DEO, 2013a). The third, four-year evaluation also concludes that of the eight 009 Action Plan goals, three were fully met, two were partially met, and three were not met. Similarly, of eighteen Action Plan recommendations, five were implemented, seven were partially or largely implemented, and six were not implemented. Of note is that there are no shortage of good recommendations for reducing nitrate contamination and improving groundwater quality in the GWMA as, for example, performing crop-specific fertilizer efficiency studies (for wheat, corn, potatoes, and onions) to assist farmers in better regulating their fertilizer use or perhaps adopting Nebraska's Central Platte Natural Resources District program to reduce groundwater nitrate. The Nebraska program requires obligatory reporting and some specific practices such as split fertilizer applications and no application of fertilizers in the fall.

A few final comments on nitrate in groundwater in Oregon. First, the leaching and transport of nitrate from a source to the groundwater is a complex process. The process includes, but is not limited to, soil characteristics (such as a soil's nitrogen binding capacity, its intrinsic leaching potential, its pH profile, its carbon content) hydrogeological features (such as rates of percolation through the vadose zone, the depth to groundwater, aquifer

flow rates) and meteorological features (such as the quantity, intensity, and timing of precipitation events and soil temperature profiles). As a corollary, in many places it may take decades to purge legacy nitrate levels from the vadose zone even with successful 'top-side' practices and programs being implemented now. Second, DEQ has made it clear that, as a direct result of funding cuts, the Department's groundwater protection abilities are compromised: "because of dwindling budget resources and other water quality priorities, DEQ's groundwater quality protection efforts have decreased significantly in the last decade and have become increasingly fragmented among multiple programs administered out of multiple offices. In the early 1990s, DEQ had 12 staff dedicated to the Groundwater program, and by the early 2000s the program staff had been reduced to five. DEQ does not have the resources to provide a coordinated groundwater quality protection program or to provide ongoing groundwater monitoring and assessment" (DEQ, 2011a). Finally, there are still options for voluntary practices.

Nitrous Oxide Inventories

Agricultural soils produce the majority of nitrous oxide emissions in the United States but overall, agriculture accounts for only about 6.9% of the total greenhouse gas emissions in the country (EPA, 2014b). According to the latest national inventory, the mean emissions from this source over a recent four-year period (2007 – 2011) were 626 Gg N₂O. In 1990 the national emissions were 587 Gg N₂O; in 2011 the national emissions were 630 Gg N₂O. Note that Gg means 'gigagram' and is equal to one billion grams. Because greenhouse inventories must consider the contributions from a variety of chemical species with different greenhouse potencies, emissions data are typically calibrated to carbon dioxide equivalents (CO₂eq). In terms of carbon dioxide equivalents, the previous values would be: 194,000 Gg CO₂eq (mean, 2007 – 2011); 182,000 Gg CO₂eq (1990); 195,000Gg CO₂eq (2011). The carbon dioxide equivalent values are much larger because nitrous oxide is a very potent greenhouse gas; about 300x more potent than CO₂. EPA notes that annual N₂O emissions from agricultural soils naturally fluctuate because of annual variation in weather patterns, synthetic fertilizer use, and crop production but overall emissions from agricultural soils are nonetheless estimated to be 8.5 percent higher in 2011 than in 1990. Of interest is the greenhouse gas emissions contributed directly from synthetic fertilizers. For the same four-year period (2007 – 2011) the mean emissions value from synthetic fertilizers is reported by EPA as 52,400 Gg CO₂eq.

In Oregon, greenhouse gas emissions are mapped to four, 'in-boundary' sectors: (1) transportation, (2) residential and commercial, (3) industrial, and (4) agricultural. DEQ estimates that the mean quantity of greenhouse emissions for a recent 20-year period (1990 – 2010) was 65,800 Gg CO₂eq (DEQ, 2013b). Contributions from each sector follow the order above (i.e., transportation contributed the most; agriculture the least). In 1990 the estimated total quantity of greenhouse emissions was 56, 200 Gg CO₂eq. In 2010 the estimated total quantity of greenhouse emissions was 62,800 Gg CO₂eq. Most of the greenhouse gas emissions from agricultural activities in the state are in the form of methane and nitrous oxide, not carbon dioxide. DEQ estimates that the mean emissions from agricultural activities for a recent 20-year period (1990 – 2010) were 5,500 Gg CO₂eq. Of this total, about 2,000 Gg CO₂eq. is from the nitrous oxide generated by the topical application of synthetic nitrogen fertilizers Another 2,000 Gg CO₂eq. is from the methane that results from enteric fermentation (i.e. the digestion of feed from livestock). The remaining quantities result from the various agricultural practices such as urea fertilization, liming of soils, and residue burning. Currently, agriculture contributes about 8.4% to the State's total greenhouse emissions.

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