



# Fertilizer efficiency in wheat is reduced by ozone pollution



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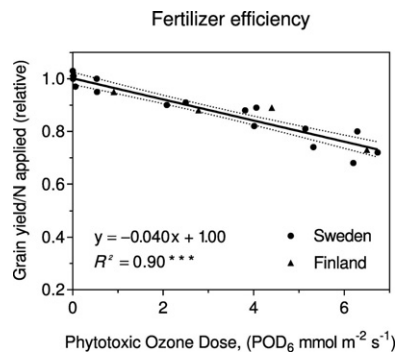
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## HIGHLIGHTS

- Ozone reduces N fertilizer efficiency with respect to protein and grain yield in wheat.
- Also P and K fertilizer is less efficiently used.
- Translocation of nitrogen to grains is negatively affected by ozone.
- Ozone pollution may increase the risk for nitrate leaching and N<sub>2</sub>O emissions.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Inefficient use of fertilizers by crops increases the risk of nutrient leaching from agro-ecosystems, resulting in economic loss and environmental contamination. We investigated how ground-level ozone affects the efficiency by which wheat used applied nitrogen (N) fertilizer to produce grain protein (NE<sub>p</sub>, N efficiency with respect to protein yield) and grain yield (NE<sub>y</sub>, N efficiency with respect to grain yield) across a large number of open-top chamber field experiments. Our results show significant negative ozone effects on NE<sub>p</sub> and NE<sub>y</sub>, both for a larger data set obtained from data mining (21 experiments, 70 treatments), and a subset of data for which stomatal ozone flux estimates were available (7 experiments, 22 treatments). For one experiment, we report new data on N content of different above-ground plant fractions as well as grain K and P content. Our analysis of the combined dataset demonstrates that the grain yield return for a certain investment in N fertilizer is reduced by ozone. Results from the experiment with more detailed data further show that translocation of accumulated N from straw and leaves to grains is significantly and negatively affected by ozone, and that ozone decreases fertilizer efficiency also for K and P. As a result of lower N fertilization efficiency, ozone causes a risk of increased N losses from agroecosystems, e.g. through nitrate leaching and nitrous oxide emissions, a hitherto neglected negative effect of ozone. This impact of ozone on the N cycle implies that society is facing a dilemma where it either (i) accepts increased N pollution and counteracts ozone-induced yield reductions by increasing fertilization or (ii) counteracts N pollution under elevated ozone by reducing fertilization, accepting further yield loss adding to the direct effect of ozone on yield.

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## 1. Introduction

Tropospheric ozone is known to reduce yields of several sensitive crops (Ashmore, 2005) and present ambient ozone concentrations

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[O<sub>3</sub>] have been shown to negatively affect wheat grain yield (Pleijel, 2011). Protein yield (protein mass per unit area) is also significantly negatively affected by ozone, although to a lesser extent than grain yield (Broberg et al., 2015; Grunhage et al., 2012). The effect on grain protein yield is evidence that applied nitrogen (N) fertilizer is less efficiently used under elevated ozone. This aspect has, however, not been explored in a consistent manner across experiments. Moreover, the other two key nutrients in crop fertilization, phosphorus (P) and potassium (K), have been considered to an even more limited extent in investigations of ozone effects on crops. In some studies where the effect of ozone on grain concentrations of these elements was reported (Fuhrer et al., 1990; Vandermeiren et al., 1992) the application rate was not. Recently, Broberg et al. (2015) showed that over the range of available experiments in the literature, although the concentration of P and K was positively influenced by ozone, the yield of these elements was significantly negatively affected. This indicates that ozone reduces fertilizer efficiency not only with respect to N but also to P and K.

There are two different aspects of N fertilizer efficiency. The first is to what extent applied N is returned as grain protein, here denoted NE<sub>P</sub> (N efficiency with respect to protein yield). A second measure of N efficiency is the return in grain yield from a certain N application, denoted NE<sub>Y</sub> (nitrogen efficiency with respect to grain yield). Reductions in NE<sub>P</sub> and NE<sub>Y</sub> both have strong implications for agro-economy and food security, as well as environmental problems associated with potentially increased ecosystem N losses. At the farm-scale, the farmer would suffer economically from a reduced return of a given investment in fertilizers. The environment suffers because when a smaller fraction of an added nutrient, in particular N, is acquired by the harvested plant parts, more is left to potentially leave the ecosystem through other processes. These include nitrate (NO<sub>3</sub><sup>-</sup>) leaching and stimulation of nitrification and denitrification, leading to increased losses of added N as nitrogen gas (N<sub>2</sub>) (Di and Cameron, 2002) and emissions of the highly potent greenhouse gas nitrous oxide (N<sub>2</sub>O) (Mosier et al., 1998).

There is evidence in the scientific literature that ozone can influence important processes below the soil surface in wheat cultivation including the rhizosphere environment. Ozone has been shown to reduce soil microbial carbon and alter microbial function and composition (Chen et al., 2015), reduce soil root activity (Chen et al., 2008) and negatively affect processes such as nitrogen rhizodeposition, which was decreased by ozone in wheat cultivation and may influence both the current and subsequent crop (Cao et al., 2016). In a free air ozone enrichment experiment (Wu et al., 2016) nitrogen cycling including soil N transformation rates were affected, more so in wheat cultivars with higher ozone sensitivity than in less sensitive cultivars. All these changes could influence soil nutrient availability and uptake by the plants as well as the carbon dynamics of the agroecosystem.

In this paper we analyze the effect of ozone on fertilizer efficiency, an ozone impact hitherto neglected. We also investigate, for one experiment where such data were available, the influence of ozone on the translocation of accumulated plant N to grains. Our first hypothesis was that fertilizer efficiency, both in terms of NE<sub>P</sub> and NE<sub>Y</sub>, would be reduced by ozone. Secondly, we hypothesized that the allocation of N from non-reproductive plant parts (straw + leaves) to the grains would be negatively affected by ozone as a consequence of ozone-induced pre-mature senescence (Gelang et al., 2000; Grandjean and Fuhrer, 1989).

## 2. Materials and methods

### 2.1. Combined analysis of ozone effects on N fertilizer efficiency based on published data

Web of Science was used to search all peer-reviewed literature published between 1980 and 2015 for experiments with wheat grown under manipulated ozone exposure (>4 weeks). Experiments with field grown crops were included where data on (i) grain yield and protein concentration, (ii) N application rate, and (iii) daytime 7-h mean

[O<sub>3</sub>] (hereafter denoted as M7) and/or the POD<sub>6</sub> (Phytotoxic Ozone Dose, Grunhage et al. (2012)) were reported or made available from authors. If the daytime [O<sub>3</sub>] was reported as the 12-h mean, this was converted to M7 using a conversion factor of 1.041 (details in Broberg et al. (2015)). NE<sub>P</sub> was calculated as the ratio between grain N harvested and N applied, and NE<sub>Y</sub> as the ratio between grain yield and N applied. For the relationship with M7 we found 21 experiments with 70 experimental treatments, conducted in seven countries on three continents. The corresponding numbers for POD<sub>6</sub> were 7 experiments, 22 treatments and 2 countries. The references and details for these experiments are presented in Supplementary Table S1.

The POD<sub>6</sub> index represents the accumulated stomatal ozone uptake by the sunlit leaves (Grunhage et al., 2012) above a threshold of 6 nmol m<sup>-2</sup> s<sup>-1</sup>, based on hourly data (LRTAP Convention, 2010). For POD<sub>6</sub>, stomatal conductance is estimated from phenology, vapor pressure deficit, temperature and solar radiation as described by Grunhage et al. (2012).

NE<sub>P</sub> and NE<sub>Y</sub> for a treatment in a particular experiment were related to that estimated for zero ozone exposure (M7 and POD<sub>6</sub>, respectively) using linear response extrapolation (Fuhrer, 1994). At zero exposure, the response variable was set to take the value of 1 on a relative scale, i.e. it was assumed that there was no ozone effect associated with zero exposure in each experiment. Experiments with only two observations and an M7 range (difference between highest and lowest ozone treatment) smaller than 15 ppb were excluded to avoid the uncertainty in the determination of the intercept and the associated response extrapolation, since random effects become large in relation to the difference in exposure for such experiments. After this transformation, the data from all experiments were combined to derive exposure-response relationships. The methodology for the calculations, including the regression method for defining relative yields for individual experiments, has been described in more detail earlier (Grunhage et al., 2012).

### 2.2. Analysis of N, P and K fertilizer efficiency and N translocation based on one experiment

For one experiment with field grown wheat (cultivar: Dragon) in open-top chambers conducted at Östads säteri in south-west Sweden (N57°54', E12°24'), the fertilizer efficiency for P and K and the shoot N fraction remaining in non-reproductive organs at harvest were analyzed. The experimental setup has been described in detail by Gelang et al. (2000). This experiment had five ozone treatments (charcoal filtered air, non-filtered air and non-filtered air with 3 different levels of ozone added), each treatment consisting of five replicate open-top chambers. Application rates of N, P and K were 120, 23 and 40 kg ha<sup>-1</sup>, respectively. The N concentration of stored grain, leaf and straw samples from this experiment were analyzed for this paper using a CHNS-O analyzer (model EA 1108, Fison Instruments, Italy), while P and K concentrations were determined using Inductively Coupled Plasma (ICP) Mass Spectrometry using a 1 g split digested in HNO<sub>3</sub>, then Aqua Regia (Basic Suite 1VE1; ACME Analytical Laboratories, Vancouver, BC, Canada). The samples were dried at 70 °C until constant mass after harvest and stored in closed containers under dry and dark conditions. In addition to NE<sub>P</sub> and NE<sub>Y</sub>, the fertilizer efficiency with respect to P and K were also analyzed. The fraction of N remaining in non-reproductive parts of the shoot at harvest was calculated. Data were analyzed using linear regression with ozone exposure expressed as the daytime average concentration.

## 3. Results

### 3.1. Combined analysis of ozone effects on NE<sub>P</sub> and NE<sub>Y</sub> based on published data

There was a negative and highly significant relationship between relative NE<sub>P</sub> and M7 (Fig. 1a). There were no obvious differences in

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