Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22498

117 (2018) 267–271
June

Use of carbon footprint to assess CO_2 and N_2O emissions during the production of nitrogen fertilizers

Krzysztof Dziuba[a], Martin Todorow[a], Radosław Góra[a], Marta Gabryszewska[b,*], Marta Kijeńska[b], Barbara Gworek[b], Andrzej Barański[b], Anna Bojanowicz-Bablok[b], Lidia Tokarz[b]

[a]*Grupa Azoty Zakłady Azotowe 'Puławy' S.A. (GA ZAP), Puławy, Poland, Tel. +48 (81) 565 23 14; email: krzysztof.dziuba@grupaazoty.com (K. Dziuba), Tel. +48 (81) 886 34 31; emails: martin.todorow@grupaazoty.com (M. Todorow), radoslaw.gora@grupaazoty.com (R. Góra)*
[b]*Institute of Environmental Protection – National Research Institute, Warsaw, Poland, Tel. +48 (22) 37 50 543; email: marta.gabryszewska@ios.edu.pl (M. Gabryszewska), Tel. +48 (22) 37 50 548; email: marta.kijenska@ios.edu.pl (M. Kijeńska), Tel. +48 (22) 37 50 503; email: barbara.gworek@ios.edu.pl (B. Gworek), Tel. +48 (22) 37 50 534; email: andrzej.baranski@ios.edu.pl (A. Barański), Tel. +48 (22) 37 50 507; email: anna.bojanowicz-bablok@ios.edu.pl (A. Bojanowicz-Bablok), Tel. +48 (22) 37 50 572; email: lidia.tokarz@ios.edu.pl (L. Tokarz)*

Received 29 January 2018; Accepted 10 May 2018

ABSTRACT

Fertiliser production makes a significant contribution to energy consumption and greenhouse gas emissions. The analysis of emission factors was carried out on a data set spanning from 2013 to 2015 for the whole chain of fertiliser production from raw materials up to the final products – ammonium nitrate, ammonium sulphate, urea in prilled form and liquid fertilisers based on them. The carbon footprint was calculated in compliance with the Standard ISO 14067:2013. The calculations were based on the gate-to-gate analysis. Analysis showed carbon footprint reduction after technological modifications – modernisation of a Benfield section, for example, absorption of gaseous CO_2 in propylene carbonite and potassium carbonite solutions, with the recovery of the pure CO_2, resulting in reduction of energy consumption from 35.3 to 33.3 GJ/Mg NH_3 – change of the N_2O decomposition catalysts, resulting in reduction of N_2O emission factor from 2 to 0.9 kg N_2O/Mg HNO_3. Life cycle assessment is a useful tool, which can be used in the decision-making process for factory modernisation and improvement the production processes.

Keywords: Fertiliser; Ammonia; Emission factor; Energy consumption; Greenhouse gases

1. Introduction

The reasons for the increasing use of fertilisers in agriculture are growing population as well as and the increased demand for raw materials and renewable energy as biofuels [1,2]. The growth in N fertiliser consumption exceeds the corresponding increase in crop yield [3]. During fertiliser production significant amounts of energy are consumed and carbon dioxide (CO_2) and other greenhouse gases (GHGs) are emitted [4–6].

Park et al. [7] indicated fertiliser production as one of five dominant industrial branches influencing the climate change. Goucher et al. [8] demonstrated that wheat cultivation with the use of ammonium nitrate (AN) fertiliser may be considered responsible for more than 50% of total impact of

* Corresponding author.

Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

the loaf of bread production on the environment. The scale of the influence of fertiliser usage on the environment is so big that even its small decrease may be substantial.

Carbon footprint (CF) allows us to take into account all the factors which may have an impact on the environment during the entire life time of product [9,10]. The gate-to-gate approach was selected to verify a possibility of the decrease of the fertiliser impact on the environment. The gate-to-gate analysis focuses on one process or stage and ignores all the steps which precede or follow it.

The question is what kind of actions can be undertaken by the largest Polish and the second largest in the EU manufacturer of nitrogen fertilisers to reduce the CF of its products?

2. Materials and methods

Data from 2013–2015 were used to determine the GHG emission factors for the fertiliser production by the Grupa Azoty 'Puławy' S.A. (GA ZAP) plant. The GA ZAP is located in central Poland in Lubelskie Voivodeship. It is the biggest plant production of nitrogen fertilisers in Poland. Intermediate products and fertilisers are manufactured on the site.

CF was calculated for the following fertilisers:

- ammonium nitrate,
- ammonium sulphate (AS),
- urea in prilled form,
- aqueous solution of urea and AN (UAN 32),
- aqueous solution of urea and AS (UAS), and
- UAN 32 and UAS solutions.

In terms of energy consumption, their manufacturing involves the use of electrical energy as well as that of medium- and high-pressure process steam. Introduced in 2011, technological modification revamping of a Benfield section in the natural gas steam reforming unit has significantly reduced the energy consumption. Natural gas is the main constituent of the processes stream, used in the synthesis of ammonia, as a fuel and a substrate. Another important fuel is bituminous coal, which is burned in the combined heat and power plant to generate process steam and electrical energy. The level of the own-produced electrical energy being insufficient, additional electrical energy has to be purchased from the Polish national power grid.

The CF of selected fertilisers was calculated according to the Standard ISO 14067:2013 [11]. The gate-to-gate approach was used, where only inputs and outputs associated with the processes within the production site were included. The factors were calculated for the following processes:

- synthesis of ammonia,
- production of nitric and sulphuric acids, and
- production of fertilisers.

Emissions from both off-site and on-site energy production were taken into account. The calculations of the emission factors for individual processes, based on the company's European Union Emission Trading System (EU ETS) monitoring data, were conducted using 'Fertilizers Europe' methods. GHG emissions associated with all activities identified within the system boundaries were in case of N_2O determined by direct measurements, and in case of CO_2 estimated according to the standard method. The following general formula (1–GA ZAP formula) was used in calculations of the CF values for the individual components, identified according to the emission sources (Fig. 1):

$$CF_j = \Sigma F_{i/j} \cdot \mathrm{EF}_{\mathrm{Fi}} + \Sigma H_{i/j} \cdot \mathrm{EF}_{\mathrm{Hi}} + \Sigma E_{i/j} \cdot \mathrm{EF}_{\mathrm{Ei}} + \Sigma G_{i/j} \cdot \mathrm{EF}_{\mathrm{Gi}} \cdot \mathrm{GWP} \quad (1)$$

CF of finished products is sum of intermediate products and energy CF (2).

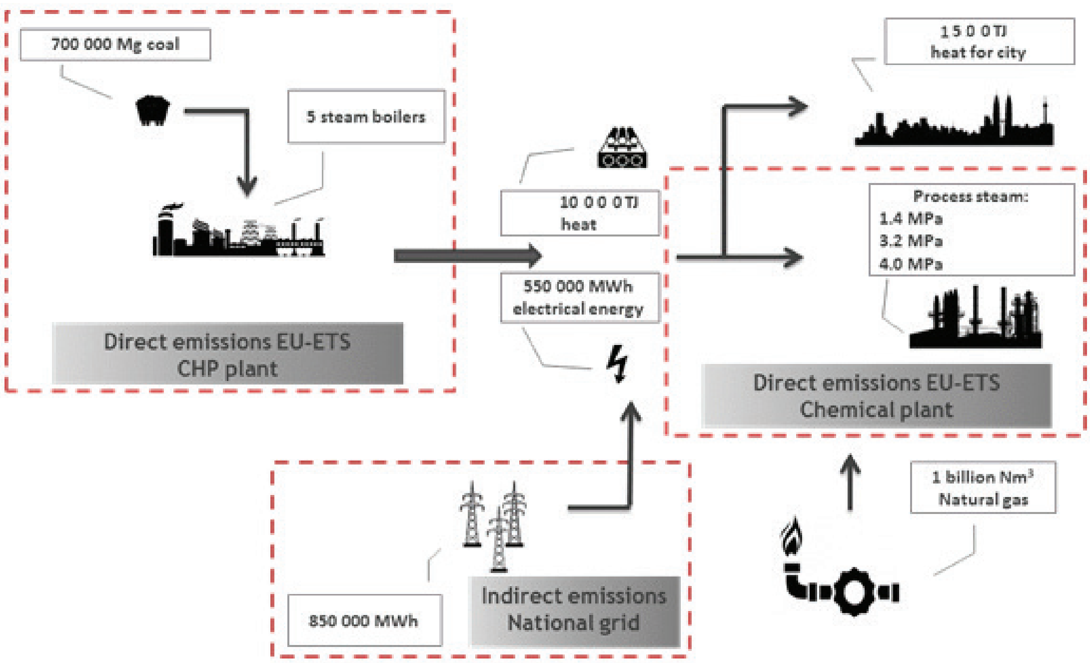

Fig. 1. GHG emission sources from fertiliser production in GA ZAP factory.

$$CF_p = \Sigma F_{j/p} \cdot CF_j + \Sigma H_p \cdot EF_H + \Sigma E_p \cdot EF_E \quad (2)$$

Above formulae are adapted to the fertiliser technological processes in GA ZAP. Prilled AN calculations of CF in 2013 are contained in Table 1. The production process includes two stages – neutralization of nitric acid with ammonia (intermediate product – AN solution) and concentration and granulation of AN melt (finished product – prilled AN).

Urea fertilisers are produced in reaction of ammonia with carbon dioxide. Also considered was the utilisation of steam generated in the production units of ammonia, nitric acid and sulphuric acid. The GHG emissions (Fig. 1) from the production of nitrate fertiliser come mainly from two sources: emission of nitrous oxide (N_2O) from nitric acid production and that of CO_2 from the use of fossil fuels as energy sources and feedstock in ammonia synthesis.

In addition to the aforementioned modification of the Benfield process, the second major technological change affecting the reduction of CF was the installation in 2012 of a new N_2O emission reduction catalyst to reduce the N_2O emission in tail gas, for example, absorption of gaseous CO_2 in propylene carbonite and potassium carbonite solutions, with the recovery of the pure CO_2. That new catalyst decomposes nitrous oxide formed in course of the nitric acid production to N_2 and O_2.

3. Results and discussion

Ammonia and nitric acid contribute significantly to total emissions, and they are the primary intermediate products used in the production of nitrogen fertilisers. The revamping of the Benfield installation in 2011 reduced energy consumption by about 10% (Fig. 2). Ammonia synthesis is a very energy-demanding process. The emissions from natural gas consumption form the main input to the ammonia CF. The CO_2 from the synthesis gas is used in urea production and is included as an emission credit.

The plants manufacturing similar fertilisers significantly differ with regard to their emission factors [12]. That is due to the differences in plant design, emission control mechanisms and feedstocks [12]. Nitrous oxide and feedstock make the largest contribution to the GHG emissions from nitric acid production. Its warming potential is 298 times higher than that of CO_2 [13,14]. Contribution of emission source for level of CF chart shows a relatively higher input from the off-site

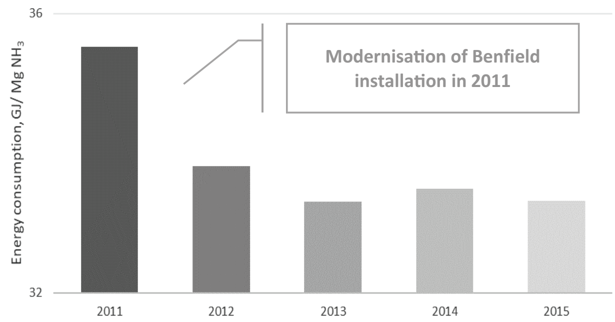

Fig. 2. Energy consumption in ammonia production in 2011–2015 in GA ZAP factory.

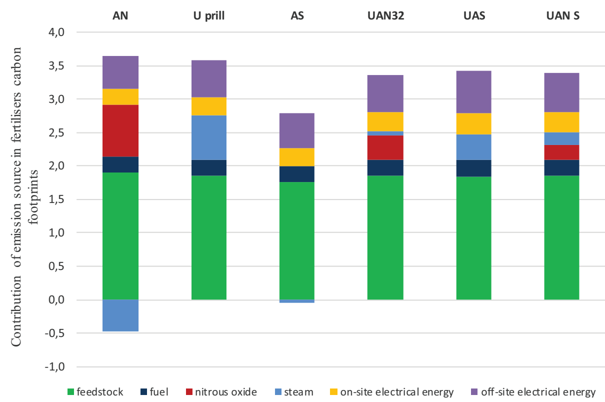

Fig. 3. Contribution of emission source for level of fertilisers carbon footprints in 2015 in GA ZAP factory.

Table 1
Example calculations of carbon footprint for ammonium nitrate prilled production process in 2013 in GA ZAP factory

Stream		Unit	Consumption (Unit/Mg AN)	EF (Mg CO_2/Unit)	CF (Mg CO_2/Mg AN)	N contented in AN (Mg N/Mg AN)	CF (Mg CO_2 / Mg N)
Ammonia	*F*	Mg	0.209	1.927	0.403	0.3501	1.151
Nitric acid	*F*	Mg	0.792	0.787	0.623	0.3501	1.779
Electrical energy	*E*	MWh	0.004	0.729	0.003	0.3501	0.009
Ammonium nitrate solution (100% conversion) carbon footprint (summary)					1.029	0.3501	2.939
AN solution	*F*	Mg	1.000	1.029	1.029	0.34	3.026
Magnesium nitrate	*F*	Mg	0.012	0.706	0.008	0.34	0.024
Electrical energy	*E*	MWh	0.026	0.729	0.019	0.34	0.056
Steam	*H*	GJ	0.499	0.103	0.051	0.34	0.150
Prilled ammonium nitrate carbon footprint (summary)					1.107	0.34	3.256

Source: GA ZAP data.
EF – Feedstock/fuel emission factor; *F* – Feedstock/fuel consumption factor; *E* – Electrical energy consumption factor; *H* – Steam consumption factor.

electrical energy production comparing with the on-site one (Fig. 3). The installation of the new decomposition catalyst results in a significant decrease in the N_2O emission factor through reduction of the concentration of N_2O in tail gas (Fig. 4). In 2013–2015 measured emissions of N_2O (see Fig. 4) were found to be lower than the EU-ETS benchmark values calculated for the listed products, heat production and fuel combustion reported by Hipolito [15]. After the construction of the new nitric acid plant the reduction in N_2O emissions from production is expected. Among the analysed fertilisers, prilled urea has the largest CF (Fig. 5). This results from the fact that carbon dioxide is bound in urea and has to be considered as a part of the emissions.

Natural gas is a raw material for ammonia production in as much as 80% of the world ammonia production [16]. That process is characterised by high energy consumption causing high CO_2 emissions and, hence, high CF values (Fig. 5). The theoretical limit for the energy consumption of that process is about 27 GJ/Mg NH_3 [17]; therefore, emissions can be reduced only to a certain level. The currently built plants producing NO_x consume about 30% less energy than those built 40 years ago [18]. In China, the process of ammonia production is energy-demanding, that is, requiring as much as 51.3 GJ/Mg NH_3-N, compared with 43.7 or 32.8 GJ Mg NH_3-N^{-1} with more advanced or the best technologies worldwide,

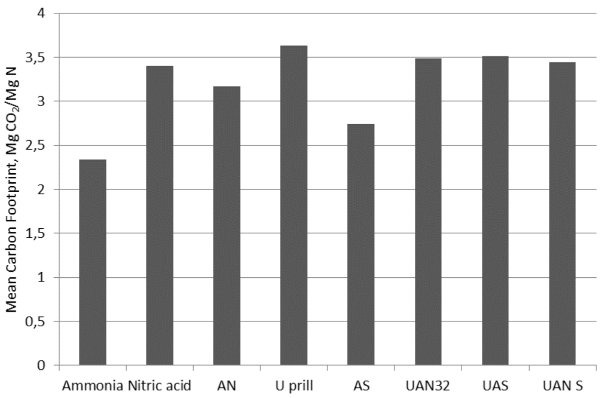

Fig. 4. Emission factor of nitrous oxide for nitric acid production in 2011–2015, in GA ZAP factory.

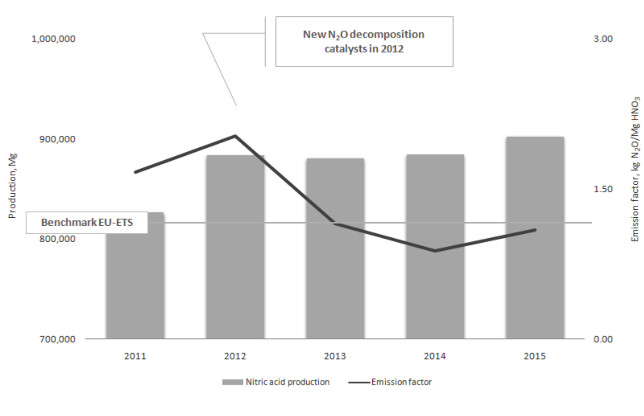

Fig. 5. Mean carbon footprints of intermediate products and fertilisers produced in GA ZAP factory, mean values for years 2013, 2014 and 2015.

with urea as the main product with energy consumption about 8.9 GJ Mg N^{-1} [19]. Research carried out by Natural Resources Canada demonstrated that the total amount of CO_2 arising from ammonia production falls within the range of 2.0–2.7 Mg CO_2/Mg NH_3-N, while the mean global level is 2.6 Mg CO_2/Mg NH_3-N [20,21]. The carbon dioxide emissions from ammonia production in 2015 in the GA ZAP plant did not exceed 1.92 Mg CO_2/Mg NH_3, whereas in the past in the Netherlands that amounted for 2.16 Mg CO_2/Mg NH_3 [22]. Through life cycle assessment (LCA) calculation it is demonstrated that new technology not only improved products but also reduced CO_2 emission to the atmosphere. The level of the carbon dioxide emissions from nitric acid production line in the GA ZAP is 0.71 Mg CO_2/Mg product. In the UAN fertiliser production line in the GA ZAP, 1.07 Mg CO_2/Mg product is released into the atmosphere, compared with 1.17 Mg CO_2/Mg product from another European plants [23]. According to EU-ETS principles, CO_2 recovered from the CO_2 removal section in ammonia plant, and subsequently used in urea production, should be included into the urea CF calculation. In the production of prilled urea, in 2015, the Polish plant released barely 1.66 Mg CO_2/Mg product into the atmosphere, while the mean level CO_2 the past emissions in Europe were of 1.85 Mg CO_2/Mg product [4]. Among the fertilisers of concern, the highest level of emission of CO_2 is related to the production of prilled urea. It should be however indicated that CO_2 is also used for urea production. This gas remains bound in the product (0.733 Mg CO_2/Mg product) until the fertiliser biodegradation on farmer's field. The highest contribution to the CF of the fertilisers of concern is due to the CO_2 emissions from the feedstock.

4. Conclusions

The technological improvements and the sustainable use of resources and energy, provide the manufacturers of fertilisers with measures to reduce GHG emissions and hence to reduce the CFs of their products.

The most important part of fertilisers' CF is emissions from the use of feedstock and the off-site energy consumption.

The actions that the company undertook to reduce CO_2 emissions were as follows:

- revamping of the Benfield section, what contributed to the decrease of the energy consumption by 10% and reduction of CO_2 emission, thus reducing the plant's overall energy consumption
- change of N_2O decomposition catalyst in tail gas, which resulted in a decrease in N_2O emissions by 50%

The investments have given positive effects by decreasing of CF to the level below 3.6 Mg CO_2/Mg N for each of the intermediates and final products.

Acknowledgement

This paper was prepared as part of the project 'Support for low-emission agriculture capable of adaptation to climate change currently and in the perspectives of 2030 and 2050' (acronym LCAgri). The Project has received funding by NCBiR from the BIOSTRATEG Programme.

Symbols

CF_j — Intermediate product j carbon footprint, Mg CO_{2eq}/Mg j
$F_{i/j}$ — Feedstock/fuel i consumption factor (natural gas, off-gas, etc.) on intermediate product j, Mg i/Mg j or 1,000 m^3 i/Mg j
EF_{Fi} — Feedstock/fuel i emission factor, Mg CO_2/Mg i or Mg CO_2/1,000 m^3 i
$H_{i/j}$ — Steam consumption factor on intermediate product j, GJ/Mg j
EF_{Hi} — Steam emission factor, Mg CO_2/GJ
$E_{i/j}$ — Electrical energy consumption factor on intermediate product j, MWh/Mg j
EF_{Ei} — Electrical energy emission factor, Mg CO_2/MWh
$G_{i/j}$ — Nitric acid consumption factor on intermediate product j, Mg HNO_3/Mg j
EF_{Gi} — Nitrous oxide emission, Mg N_2O/Mg HNO_3
GWP — Global warming potential (GWP_{CO_2} = 1, GWP_{N_2O} = 298), Mg CO_{2eq}/Mg N_2O
CF_p — Finished product p carbon footprint, Mg CO_{2eq}/Mg p
$F_{j/p}$ — Intermediate product j consumption factor on product p, Mg j/Mg p
CF_j — Intermediate product j carbon footprint, Mg CO_2/Mg j
H_p — Steam consumption factor on product p, GJ/Mg p
EF_H — Steam emission factor, Mg CO_2/GJ
E_p — Electrical energy consumption factor on product p, MWh/Mg p
EF_E — Electrical energy emission factor, Mg CO_2/MWh

References

[1] A.J. Challinor, F. Ewert, S. Arnold, E. Simelton, E. Fraser, Crops and climate change: progress, trends, and challenges in simulating impacts and informing adaptation, J. Exp. Bot., 60 (2009) 2775–2789.
[2] K. Hasler, S. Bröring, S.W.F. Omta, H.-W. Olfs, Life cycle assessment (LCA) of different fertilizer product types, Eur. J. Agron., 69 (2015) 41–51.
[3] M. Zhou, B. Zhu, N. Brüggemann, J. Bergmann, Y. Wang, K. Butterbach-Bahl, N_2O and CH_4 emissions, and NO_3^- leaching on a crop-yield basis from a subtropical rain-fed wheat-maize rotation in response to different types of nitrogen fertilizer, Ecosystem, 17 (2013) 286–301.
[4] J. Davis, C. Haglund, Life Cycle Inventory (LCI) of Fertiliser Production. Fertiliser Products Used in Sweden and Western Europe. SIK-Report No. 654, Master Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1999.
[5] J. Bellarby, B. Foereid, A. Hastings, P. Smith, Cool Farming: Climate Impacts of Agriculture and Mitigation Potential, Greenpeace, Amsterdam, the Netherlands, 2008.
[6] F. Brentrup, C. Pallière, GHG Emissions and Energy Efficiency in European Nitrogen Fertiliser Production and Use, Proc. The International Fertiliser Society, Cambridge, England. ISBN 978-0-85310-276-2, Vol. 639, 2008, pp. 1–26.
[7] Y.S. Park, G. Egilmez, M. Kucukvar, Emergy and end-point impact assessment of agricultural and food production in the United States: a supply chain-linked ecologically-based life cycle assessment, Ecol. Indic., 62 (2016) 117–137.
[8] L. Goucher, R. Bruce, D.D. Cameron, S.C. Lenny Koh, P. Horton, The environmental impact of fertilizer embodied in a wheat-to-bread supply chain, Nat. Plants, 3 (2017) 17012.
[9] J.B. Guinée, M. Gorrée, R. Heijungs, G. Huppes, R. Kleijn, A. de Koning, A. Wegener Sleeswijk, S. Suh, H. Udo des Heas, H. Bruijn, R.V. Duin, M.A.J. Huijbregts, Handbook on the Life Cycle Assessment. Operational Guide to the ISO Standards. Book Series: Eco-Efficiency in Industry and Science, Vol. 7, Kluwer Academic Publishers, Dordrecht, the Netherlands, 2002.
[10] H. Baumann, A.-M. Tillman, The Hitch Hiker's Guide to LCA. An Orientation in Life Cycle Assessment Methodology and Application, Studentlitteratur, Lund, 2004.
[11] ISO 14067:2013: Greenhouse Gases – Carbon Footprint of Products: Requirements and Guidelines for Quantification and Communication, 2013.
[12] S. Wood, A. Cowie, A Review of Greenhouse Gas Emission Factors for Fertiliser Production, 2004. Available at: https://www.researchgate.net/publication/235704822_A_Review_of_Greenhouse_Gas_Emision_Factors_for_Fertiliser_Production (Accessed 24 October 2016).
[13] IPCC, Climate Change (2007): Synthesis Report. Contribution of Working Groups I, II and II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, R.K. Pachauri, A. Reisinger, Eds., Intergovernmental Panel on Climate Change, Geneva, Switzerland, 2007.
[14] BSI, Publically Available Specification, PAS 2050:2011, Specification for the Assessment of the Life Cycle Greenhouse Gas Emissions of Goods and Services, ISBN 978 0 580 71382 8, ICS 13.310; 91.190, 2011.
[15] M.G. Hipolito, Benchmark based allocation methodologies for the EU ETS, 2014. Available at: http://www.kazccmp.org/OpenLibrary/10_20_workshop/Almaty_20_21_Oct_CL_Allocation.pdf (Accessed 14 October 2016).
[16] A. Kool, M. Marinussen, H. Blonk, LCI Data for the Calculation Tool Footprint for Greenhouse Gas Emissions of Feed Production and Utilization GHG Emissions of N, P and K Fertilizer Production, 2012. Available at: http://www.blonkconsultants.nl/wp-content/uploads/2016/06/fertilizer_production-D03.pdf (Accessed 27.10.2016).
[17] CIPEC (Canadian Industry Program for Energy Conservation): Canadian Ammonia Producers: Benchmarking Energy Efficiency and Carbon Dioxide Emissions, 2008. Available at: http://publications.gc.ca/collections/collection_2009/nrcan/M144-155-2007E.pdf (Accessed 11 July 2017).
[18] IFA, Ammonia Production: Moving Towards Maximum Efficiency and Lower GHG Emissions, 2014. Available at: https://www.fertilizer.org//images/Library_Downloads/2014_ifa_ff_ammonia_emissions_july.pdf (Accessed 18 October 2016).
[19] W. Zhang, Z. Dou, P. He, X.-T. Ju, D. Powlson, D. Chadwick, D. Norse, Y.-L. Lu, Y. Zhang, L. Wu, X.-P. Chen, K.G. Cassman, F.-S. Zhang, New technologies reduce greenhouse gas emissions from nitrogenous fertilizer in China, PNAS, 110 (2013) 8375–8380.
[20] NRCan, Canadian Ammonia Producers: Benchmarking Energy Efficiency and Carbon Dioxide Emissions, Issued by the Canadian Industry Program for Energy Conservation, Natural Resources Canada, 2007, ISBN 978-0-662-45981-1.
[21] C.S. Snyder, T.W. Bruulsema, T.L. Jensen, P.E. Fixen, Review of greenhouse gas emissions from crop production systems and fertilizer management effects, Agric. Ecosyst. Environ., 133 (2009) 247–266.
[22] K.J. Kramer, H.C. Moll, S. Nonhebel, Total greenhouse gas emissions related to the Dutch crop production system, Agric. Ecosyst. Environ., 72 (1999) 9–16.
[23] J. Kuesters, T. Jenssen, Selecting the Right Fertilizer from an Environmental Life Cycle Perspective, IFA Technical Conference, Marrakech, Morocco, 1998, p. 7.