Alfons Buekens*

Vrije Universiteit Brussel, 1050 Brussels, Belgium Email: abuekens@vub.ac.be *Corresponding author

Bogdan Z. Dlugogorski

School of Engineering and Information Technology, Murdoch University, 90 South Street, Murdoch WA 6150, Australia Email: B.Dlugogorski@murdoch.edu.au

Slawo Lomnicki

Department of Environmental Sciences, Louisiana State University, 1251 Energy Coast and Environment Bldg., Baton Rouge, LA 70803, USA Email: slomni1@lsu.edu

Shengyong Lu

State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering (ITPE), Zhejiang University, Hangzhou, Zhejiang Province 310027, China Email: lushengyong@zju.edu.cn

Kees Olie

University of Amsterdam, P.O. Box 19268, 1000 GG Amsterdam, The Netherlands Email: k.olie@upcmail.nl

Masaki Takaoka

Urban and Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyodai katsura, Nishikyo-ku, Kyoto 615-8540, Japan Email: takaoka@environ.mbox.media.kyoto-u.ac.jp

Copyright © 2016 Inderscience Enterprises Ltd.

Biographical notes: Alfons Buekens received his MSc (1964) and PhD (1967) in Chemical Engineering from Ghent University, Dept. of Petrochemical Techniques. Nominated (1969) at Vrije Universiteit Brussel and Full Professor (1975), he served as consultant in environmental and safety issues for the E.U., UNIDO, WHO, and Belgian Development Aid and as invited professor at numerous universities, including Tohoku University (2002/3). He coordinated the Cycleplast, Upcycle, and Minidip E.U.-Projects. Finally, he joined Zhejiang University in 2008, participating in R&D-work in thermal processes, flue gas cleaning and dioxins. His work was recognised by awards from the Royal Association of Flemish Engineers, the Robert De Keyser Foundation (Shell), the Coca Cola Foundation, the Körber Foundation, the Japanese Society for Feedstock Recycling, i-CIPEC, West Lake Friendship, etc.

Bogdan Dlugogorski develops industrial processes that are safe to people and the environment, particularly those related to flammability, the formation of brominated, chlorinated, and mixed-halogenated dioxins and related molecules, the emission of NOx, storage of CO_2 by mineralisation and utilisation, and nitrosation processes. He is an Immediate Past Chairman of the International Association for Fire Safety Science, and has been bestowed with the Harry C. Bigglestone Award, the R.K. Murphy Medal, the Eureka Prize for Environmental Research, the Esso Award of Excellence, and the IAFSS Philip Thomas Medal of Excellence. He holds degrees from The University of Calgary, McGill University, Université de Montréal and The University of Newcastle, Australia. He is a Chartered Professional Engineer, Fellow of Australian Academy of Technology and Engineering, and the Dean of Engineering and Information Technology at Murdoch University in Perth, Australia.

Slawo (Slawomir) M. Lomnicki is Assistant Professor of Environmental Sciences at Louisiana State University and Director of the Materials Core of the LSU Superfund Research Center.He is Co-Chair of the Executive Committee of the International Congress on Combustion By-Products and Their Health Effects, authored over 60 manuscripts in peer-reviewed journals and presented papers at numerous conferences. His expertise is in Physical Chemistry, with special emphasis on surface-driven reaction processes. His research is mostly focused on combustion processes and the resulting environmental pollutants, as well as on the reactivity of pollutants with active surfaces in the ambient environment. A comprehensive mechanism of the surface mediated formation of PCDD/Fs was developed.

Shengyong Lu received his PhD (2004) in Energy and Environmental Systems Engineering from Zhejiang University, Zhejiang, China and started to work at Zhejiang University in 2004, since 2012 as a Full Professor. His research concentrates on the generation, emission and control of trace toxic organic pollutants in solid waste disposal, developing online dioxins detection techniques and dioxins abatement, using composite catalysts as well as photochemical and mechanochemical methods to degrade dioxins.

Kees Olie studied inorganic chemistry at the University of Amsterdam and graduated in 1974 after structural and spectroscopical investigations of some PYX3 molecules. In 1975 he joined the Dept. of Environmental and toxicological chemistry at the University of Amsterdam and discovered PCDD/Fs in effluents of municipal waste incineration (1976). Since, his research centres on the formation and degradation of PCDD/Fs. After retiring from Amsterdam, he acts as Visiting Professor at Zhejiang University and in 2015 he received the Adel F. Sarofim Award.

2

Masaki Takaoka received his MSc (1993) and PhD (2001) in Chemical Engineering from the Department of Environmental Engineering, Graduate School of Engineering, Kyoto University and works as a Full Professor in Kyoto University since 2011. His interests are: solid waste treatment, disposal and management, characterisation of solid waste, development of recycling, control of micro-pollutants from thermal treatment, and development of advanced sewage sludge treatment.

1 Seveso

In 1976, following a reactor runaway, a cloud of chlorophenols contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin escaped from a chemical reactor in Seveso, close to Milan, Italy. This major incident prompted the evacuation and continued monitoring of the local population affected and also urged an unprecedented crackdown on industry, blowing away earlier economic considerations such as secrecy of supply and processes. To minimise the risks associated with storage and production, measures were necessary to prevent major accidents to occur and to ensure appropriate preparedness and response should such accidents happen. The Seveso-Directive (Directive 82/501/EEC) was amended after the lessons learned from later accidents such as Bhopal, Toulouse or Enschede, resulting into Seveso-II (Directive 96/82/EC). Later, Seveso-III (Directive 2012/18/EU) was taking into account the changes in the European Union legislation on the classification of chemicals and the increased rights for citizens to access information and justice. The Directive now applies to more than 10,000 industrial establishments where dangerous substances are used or stored in large quantities, mainly in the chemical, petrochemical, logistics and metal refining sectors (Industrial Accidents, http://ec.europa.eu/environment/seveso/).

2 Municipal solid waste incineration and other sources

Only one year after Seveso, Olie et al. (1977) discovered polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF) on fly ash and in flue gas from municipal solid waste incineration. These two unrelated events entirely changed the face of both the chemical industry (Seveso Directive) and waste incineration (cleaner combustion, cleaned flue gas). New emission limits for incinerator flue gas required a number of preventive and curative measures, including improved combustion conditions, avoiding upsets, a much deeper removal of particulate matter, of acid gases, and of semi-volatile organics, including PCDD and PCDF.

They also gave rise to unprecedented efforts to determine dioxins reliably and quantitatively, to identify their sources and emission levels and drastically reduce these. Some countries have imposed a continuous sampling and periodic analysis of PCDD and PCDF. Many more dioxins sources were discovered, in particular in metallurgical processes, some of these quite unexpected in nature or amount. Abatement and monitoring became generalised and interest at present has shifted towards more recent toxic emissions, further from emissions to immissions and eventual uptake, in particular related to their eventual impact on the food chain.

3 Global emissions

Dioxins emissions had already peaked before 1976, as follows from both stored soil and grass samples and sediment cores (Alcock et al., 1998). Today, new techniques are applied to dioxins monitoring and research, yet the research budgets in Europe and the USA started dwindling, as soon as emissions and their abatement seemed satisfactorily under control. The Belgian dioxins scandal, actually involving the dumping of a PCB charge into animal fat to be recycled, shifted emphasis towards the food chain and no longer addressed dioxins sources of formation. Once all guided emissions are controlled, the relative importance of informal and accidental burning increases. In both developing and more mature countries such open burning of waste has become the main emission source of dioxins. Today, the open burning of biomass and waste evolved into their most prominent source, and establishing reliable emission factors for ill-defined open burning cases is still a research priority.

Monitoring of dioxins is still expensive and cumbersome; continuous sampling is well established, yet the use of surrogates or other indicator substances (Lavric et al., 2005) never has convinced sufficiently to become state of the art.

4 Sources

Dioxins appear in all kinds of fire, from a mere burning cigarette to the enormous fires periodically devastating forests and bush, or – industrially – from firing coal to integrated steelworks. Since the first studies on dioxins, copper has emerged as a premium catalyst, yet the number of unknowns in such catalysis remains baffling, e.g., the role of speciation, of the matrix materials, or of other transition metals showing either synergy, or antagonism. Since Seveso, the precursor route is firmly established and confirmed in various synthesis processes involving chlorophenols and other precursors. Sintering ores, conversely, is so lean in PCDD that the de novo route obviously seems dominant. Recent research on the precursor route and the de novo synthesis pathway needs to be closer surveyed and analysed, to try to explain individual fingerprints, as appearing from the most various sources.

Finally, some more attention is still to be paid to the more recent findings in incineration and metallurgy, the evolution in techniques to prevent, adsorb, or oxidise dioxins, and those to detoxify fly ash and soil, contaminated with dioxins and other persistent organic pollutants (POPs).

5 China

For a number of years, waning interest in OECD countries has been more than compensated for by newly emerging research groups in China, a country confronted with the explosive growth of its heavy industry, including cement and steel production. Moreover, their number of incineration units is growing steadily and the air pollution emission control units still work way below their theoretical capacities, involving both dust collection and adsorption of dioxins. This also explains the large number of R&D projects in China focusing on the avoidance and abatement of dioxins.

6 Themes

The following short list of themes had been proposed for this special issue, yet room was left for a survey of health effects, related factors such as free radicals, surveying the food chain, etc. The following themes were put forward:

- Emission inventories of dioxins.
- Monitoring of dioxins.
- Open burning: main source of dioxins?
- Metal catalysis and dioxins formation.
- De novo pathways towards chlorinated aromatics and dioxins.
- Precursor route of dioxins formation: the PCDF/PCDD ratio.
- Incineration and dioxins: progress of the last 25 years.
- Cleaning flue gases from dioxins.
- Destruction of POPs and dioxins.
- The fingerprint or signature of dioxins.
- Thermodynamic aspects of the formation and destruction of dioxins.
- Chemical and physicochemical properties of dioxins.

Both review papers and case studies were welcome.

7 Contents of this special issue

This special issue opens with the invited contribution of Takumi Takasuga (Japan), titled 'GC-HRMS analysis for old and new POPs with GC-Tof/MS techniques'. This paper briefly relates some important technical developments and achievements in the analysis of dioxins as well as old and new POPs. Seven of the papers are included in this issue; the remaining papers will appear in a later issue of this journal.

7.1 General

Three introductory inputs relate to:

- 1 the vast literature on dioxins at large
- 2 evaluating the response to notorious industrial incidents, relating to dioxins and dioxin-like PCBs
- 3 the extraction methods for determining PCBs and chlorobenzenes in fly ash and sludge.

In 'Global research activities on dioxins and dioxin-like compounds', Can-Güven and Gedik (Turkey) fathom the extent of dioxins literature from 1970 to 2015, based on searching Web of Science; a total of 18,805 publications were examined and classified

according to bibliometric criteria, i.e., document type, language, publication outputs, distribution of journals, subject category, countries, institutions, title words, author keywords, and keywords plus. Stimulated mostly by legislative interventions or regulations, the annual number of publications has steadily been rising. *Chemosphere* was the journal with most articles and 'Environmental Science and Ecology' and 'Toxicology' were the most common subject/topic categories. The most productive country and institution were, respectively, the USA and US EPA.

B. Hens (Belgium), P. Dyke (UK) and L. Hens (Belgium) discuss 'What can we learn from 'dioxin incidents?'. These include the widespread contamination caused by applying dioxins-contaminated chemicals, as well as accidents in industry, inappropriate waste management and a series of instances where specific contamination of food or animal feed has occurred. The authors review selected incidents and discuss how these helped to frame policy responses and how regulation and monitoring gradually evolved. The authors also comment on work to assess their impact on human health.

In the next issue, Sun et al. (China and Japan) will study the 'Effect of water content on microwave-assisted extraction to analyse PCBs and chlorobenzenes in actual fly ash and sludge from municipal solid waste incineration'. Compared with the conventional Soxhlet extraction, microwave-assisted extraction shows unique advantages such as greatly reduced extraction time and solvent volume during the extraction of high chlorinated homologues. Starting from this paper, further research seems warranted to try and optimise this promising method and additionally investigate in more depth the impact of sample characteristics, and extraction time and conditions.

7.2 Formation and suppression

Already during the 1990s, numerous studies were conducted on the de novo synthesis of dioxins and other organohalogens. Those featuring a fixed bed of fly ash are extensively reviewed by Zhang and Buekens (China) in 'De novo synthesis of dioxins: a review'. Numerous experimental variables (temperature, time, carbon, chlorides, and catalyst in (model) fly ash, and oxygen content in the reaction atmosphere) are considered, along with their effects on de novo formation. Also, attention is paid to the chlorophenol precursor route occurring in this framework of de novo tests.

A second paper by the same authors scrutinises 'De novo synthesis in iron ore sintering' as a case study, with special attention for an extensive experimental data set, generated during the EU Programme Minimisation of Dioxins in Thermal Industrial Processes (MINIDIP).

A contrasting view will be presented by Lomnicki (USA) in his forthcoming contribution 'Surface-catalysed PCDD/Fs formation from precursors: high PCDF yields do not indicate a de novo mechanism'. This thesis is supported tentatively by results from experimental research, suggesting that the PCDD to PCDF ratio in the catalytic system studied is determined by its ratio of chlorinated benzenes (CBz) to chlorinated phenols (CP). Results are reported on PCDD/F formation from the catalytic conversion of a gas phase mixture of 2-MCP and 1,2-DCBz supplied in variable proportions. These three papers all address de novo synthesis experiments, as well as the precursor route, starting from carbon on the one hand, chlorophenols and chlorobenzenes, the two most cited precursors, on the other hand.

The next paper considers an unusual and intriguing model substance, a combining of a PCB-structure, another potential precursor, with substitution by both chlorine and

bromine. Song et al. (Australia) experimentally investigated the various 'Toxicants formed in fires of 4-bromo-4'-chlorobiphenyl'. These toxic compounds are identified by means of various analytical techniques and a sharp maximum in the formation of dibenzofuran derivatives and other compounds is found below 700°C. Gas chromatography-quadrupole mass spectrometry (GC-QMS), gas chromatography-quadrupole time of flight mass spectrometry (GC-QTofMS), Fourier transform infrared spectroscopy (FTIR) and ion chromatography (IC) all served to analyse the volatile and semi-volatile organic compounds (V/SVOCs), including mixed halogenated dibenzo-p-dioxins and dibenzofurans (PXDD/Fs), gas products, and HBr/HCl, respectively.

The partition between gas phase and particulate matter is an important factor at the level of fly-ash separation, its effect on PCDD/F in flue gas, and then their further treatment by either adsorption or oxidation. Liu et al. (China) study the clean gas and propose a 'Comparison and relationship of polychlorinated dibenzo-p-dioxins and dibenzofuran levels between stack gas and fly ash samples from waste incinerators'.

For the first time, Lu et al. (China) sampled PCDD/F in an externally circulating fluidised bed MSWI-unit, at four vastly different temperature levels. In 'Levels and profiles of dioxins from circulating fluidised bed incineration', these levels remained rather low at the exit of furnace (850°C) and the end of post-combustion (450°C), the bulk of PCDD/F appearing largely while the flue gas flows through the convection section of the waste heat boiler. Remarkably, the homologue profile varies slightly only, yet within these homologue groups the isomer signature varies strongly with temperature. This feature will be treated in more detail in a future paper.

Finally, this section concludes with some PCDD/F-measurements and fingerprints from two industrial plants in Poland, one relating to iron ore sintering, the others monitoring a secondary copper smelter during an entire operating cycle. After an extensive review of relevant literature, Wielgosinski et al. describe their findings in their paper 'Dioxin emission from metallurgical processes'.

7.3 Abatement and destruction

There are several most interesting entries examining the various solutions to treat or reduce the formation of dioxins or PCBs gathered under the two topics of 'abatement and destruction'. Discussed are adsorption of various surrogates of PCDD/F on activated carbons, the catalytic destruction of gas phase PCDD/F, inhibition by means of urea addition, the thermal desorption of contaminated soils and, finally, the possibilities offered by biological treatment.

Takaoka et al. (Japan) study the suppression of the extra formation of dioxins (and NOx) in a contribution: 'Simultaneous control of polychlorinated dibenzo-p-dioxins/dibenzofurans, polychlorinated biphenyls and nitrogen oxide in flue gas using urea'. Their studies relate to the technical possibility of filtration of fly ash at high temperature.

Grisdanurak et al. (Thailand) examine the 'Capture of dioxin derivatives on activated carbons: breakthrough curve modelling and isotherm parameters' as a practical and modelling application of chemical engineering principles in gas cleaning. The authors study the breakthrough curves of various PCDD/F surrogates for several types of activated carbon and derive important adsorption parameters from their findings.

In an experimental study Du et al. (China) treat the 'Catalytic oxidation of 1,2-DCBz over V_2O_5/TiO_2 -CNTs catalysts: the effect of water'. The study fits into a number of studies systematically studying the lowering of operating temperature during the catalytic oxidation of PCDD/F or of its surrogates.

Li et al. review the technical methods for 'Thermal desorption for remediating PCB-contaminated soil'. The following parameters are considered: temperature and retention time, particle size, carrier gas, heating rate, desorption and decomposition. An important feature addressed is the off-gas treatment, consecutive to the thermal desorption.

8 **Reviewers**

Apart from members of our editorial board several external reviewers were so kind to ensure a critical review of one or (generally) more papers. Several of these reviewers substantially improved particular papers, so that they received a special acknowledgement for their contributions.

Special thanks are due to the following scientists, cited in alphabetical order:

- Ruud Addink (NL/USA)
- Mohammednoor Altarawneh (Australia)
- Moobeen Chang (Taiwan)
- Mariusz Cieplik (The Netherlands)
- Patrick Dyke (UK)
- Fukuya Iino (Japan/Austria)
- Jinrong Liu (China)
- Robert Louw (NL)
- Don Lucas (USA)
- Sylwia Oleszek (Poland/Japan)
- Kees Olie (the Netherlands)
- Mi Yan (China)
- Jürgen Vehlow (Germany)
- Roland Weber (Germany)
- GrzegorzWielgosinski.

References

- Alcock, R.E., McLachlan, M.S., Johnston, A.E. and Jones, K.C. (1998) 'Evidence of PCDD/Fs in the environment prior to 1900 and further studies on temporal trends', *Environ. Sci. Technol.*, Vol. 32, No. 11, pp.1580–1587.
- Industrial Accidents [online] http://ec.europa.eu/environment/seveso/ (accessed 8 June 2016).
- Lavric, D., Konnov, A.A. and De Ruyck, J. (2005) 'Surrogate compounds for dioxins in incineration. A review', *Waste Management*, Vol. 25, No. 7, pp.755–765.
- Olie, K., Vermeulen, P.L. and Hutzinger, O. (1977) 'Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in The Netherlands', *Chemosphere*, No. 6, No. 8, pp.455–459.