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Addendum to "Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment" (Concawe Report 4/12); Addition of more recent datasets

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Addendum to “Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment” (Concawe Report 4/12); Addition of more recent datasets

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ABSTRACT

Ether oxygenates are added to certain gasoline (petrol) formulations to improve combustion efficiency and to increase the octane rating. In 2012 Concawe published the findings of research to support effective environmental management practices for gasoline ether oxygenates (GEO) in Concawe Report 4/12 “Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment” (Concawe, 2012). This addendum report provides an updated appraisal of trends in 1999-2015 fuel GEO content as well as trends in the ethanol (EtOH) content of gasoline from 2010-2015.

KEYWORDS

Ether oxygenates (EO), gasoline ether oxygenates (GEO), methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), di-isopropyl ether (DIPE), and tertiary hexyl ethyl ether (THxEE), tertiary butyl alcohol (TBA), GEO use, GEO occurrence in Europe, Ethanol (EtOH), fuel, new dataset

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SUMMARY

Ether oxygenates (EO) are added to certain gasoline (petrol) formulations to improve combustion efficiency and to increase the octane rating. In 2012 Concawe published the findings of research to support effective environmental management practices for gasoline ether oxygenates (GEO) in Concawe Report 4/12 “Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment” (Concawe, 2012). This addendum report provides an updated appraisal of trends in 1999-2015 fuel GEO content as well as trends in the ethanol (EtOH) content of gasoline from 2010-2015.

The updated dataset indicates that average concentration of the sum of ethyl tertiary butyl ether (ETBE) and methyl tertiary butyl ether (MTBE) in EU gasoline remained approximately constant between 1999-2009 and 2010-2015. However, there was a shift towards higher ETBE concentration and lower MTBE concentration which continued the trend observed in Concawe Report 4/12. Average di-isopropyl ether (DIPE) and tertiary butyl alcohol (TBA) concentrations remained low over the period 2010-2015 (average concentration <0.01 m/m%). The use of TAME as a GEO continued in Finland but only minor concentrations were present elsewhere (average concentration <0.5 m/m%).

Trend analysis of 2010 and 2015 data indicates an overall decrease in the sum of ETBE and MTBE content (from 4.66 to 3.68 m/m%), and an increase in EtOH content (from 3.42 to 4.60 m/m%). Prior to 2010 the average EtOH concentration in EU gasoline was 0.79 m/m%.

1. BACKGROUND

Ether oxygenates are added to certain gasoline (petrol) formulations to improve combustion efficiency and to increase the octane rating. In 2012 Concawe published the findings of research to support effective environmental management practices for gasoline ether oxygenates (GEO) by Concawe members in Concawe Report 4/12 "Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment". The report includes a literature review on the fate and transport characteristics of GEO and also data on the production capacity and use of methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), di-isopropyl ether (DIPE), tertiary amyl ethyl ether (TAEE), tertiary hexyl methyl ether (THxME), and tertiary hexyl ethyl ether (THxEE), as well as the associated tertiary butyl alcohol (TBA) in 30 countries (27 EU countries and Croatia, Norway and Switzerland). The database used to produce Report 4/12 was from SGS (Société Générale de Surveillance) and contained information from 1,239 sampling events on MTBE, ETBE and TBA, and 650 sampling events on TAME and DIPE (Concawe, 2012).

In the 5 years since Concawe Report 4/12 was published additional data has been compiled by the Concawe Fuels and Emissions Management Group (FEMG). This addendum report updates the findings of Report 4/12 with this more recent data, which is as follows:

1. Concawe FEMG-STF-24 2010 European Fuel Survey
2. SGS Summer 2010 to Winter 2011/2012 European Fuel Survey
3. Concawe FEMG-STF-24 2015 European Fuel Survey

In addition to the above 2010-2015 datasets, this report includes SGS survey data on EU gasoline ethanol (EtOH) concentrations from 2006-2009.

2. MAIN FINDINGS FROM CONCAWE REPORT 4/12 IN RELATION TO GEO CONTENT OF EU GASOLINE

2.1. GENERAL TRENDS

The 2012 Concawe study (as presented in Concawe Report 4/12) found that MTBE was detected in premium unleaded (PUL) gasoline in all EU 27 in the period 2004-2009, and that ETBE use in PUL was less widespread than MTBE in the same period. The highest ETBE concentrations (5-12 m/m%) in PUL gasoline were found in France, Spain, Hungary and Austria. TAME was detected in PUL and premium unleaded plus (PULP) gasoline in concentrations from 1 to 3 m/m% in Cyprus, Finland, Greece, Italy, Malta, Romania and Slovenia. DIPE was detected only in 7 out of 650 samples at concentrations below 1 m/m%. Trace quantities of TBA (0.01-0.03 m/m%) were detected in many EU countries.

Average (mean), median and maximum concentrations of GEOs detected in individual sampling rounds in those countries covered by the SGS fuel survey (as presented in Concawe Report 4/12) are presented in **Table 1**. The 2012 study found that GEO use had switched from MTBE to ETBE in certain countries, and also that the total GEO content of gasoline had decreased in certain markets (possibly in response to the increased use of EtOH in gasoline).

Table 1: EO in gasoline, from winter 1999/2000 to summer 2009, in 27 European countries. Mean, medium and maximum reported concentrations (m/m%) from a SGS database. (Concawe, 2012).

	Ether Oxygenates				
	MTBE	**ETBE**	**TAME**	**DIPE**	**TBA**
Total number of sampling events (n)					
	1,239	1,239	650	650	1,239
Mean (average) concentration in all European gasoline samples in 1999-2009 (m/m%)					
	5.39	0.91	0.29	<0.01	0.03
Median concentration in all European gasoline samples in 1999-2009 (m/m%)					
	4.25	<0.01	<0.01	<0.01	0.01
Maximum concentration observed in individual sampling rounds (m/m%)					
Concentration (m/m%)	20.43	15.50	11.22	0.88	1.03
Gasoline type	PULP	PUL	PUL	PULP	PULP
Period	Summer 2001	Winter 2008/2009	Winter 2007/2008	Winter 2002/2003	Winter 2000/2001
Country	Romania	France	Finland	Greece	Switzerland

2.2. REGIONAL VARIATION

France, Poland and the UK had a relatively low concentration of MTBE in PUL gasoline. The ETBE concentration in PUL was high (5-12 m/m%) in France, Spain, Hungary and Austria, whereas in Germany the ETBE concentration in PUL was decreasing. TAME was reported in PUL and PULP gasoline in Cyprus, Finland, Greece, Italy, Malta, Romania and Slovenia, at a concentration of 1 to 3 m/m% with the highest concentration detected in Finland. This is likely related to the TAME production facilities in Finland, Greece and Italy. DIPE was detected in only 7 out of 650 samples in Bulgaria, Greece, Malta, Italy and Sweden in a concentration below 1 m/m%. Trace amounts of TBA (0.01-0.03 m/m%) are detected in many EU countries. In 2012 Denmark was the only country that had phased out the use of MTBE.

An evaluation was completed in Concawe Report 4/12 for the countries with highest fuel consumption. The main findings were as follows:

- **Finland.** Finland was one of the few producers of TAME and TAEE, and TAME was the dominant GEO used in gasoline. The production capacity in 2007 exceeded the national GEO demand in gasoline by about 50%.
- **France.** ETBE dominated the French GEO market and France was one of the first countries to introduce ETBE. MTBE was used only in small amounts. The GEO production capacity in 2007 was below the national demand.
- **Germany.** In the past MTBE was widely used in PUL and PULP gasoline. Since 2007 the ETBE concentration in PUL had been higher than the MTBE concentration. However, the ETBE concentration in PUL gasoline had dropped to less than 2% since 2008, due to direct blending of EtOH in gasoline. GEO production capacity exceeded national demand.
- **Italy.** MTBE was mostly used in the Italian market, but ETBE use was increasing. The production capacity exceeded national demand.
- **Spain.** ETBE dominated the Spanish GEO market. Together with France, Spain was one of the first countries to introduce ETBE. MTBE was used only in small amounts. The production capacity in 2007 was sufficient to meet national demand.
- **United Kingdom.** GEO concentrations in UK gasoline were generally low, up to 1-2%, and mostly represented by MTBE. TAME was also applied in some instances. The production capacity in 2007 was sufficient to meet national demand.

3. UPDATED FINDINGS TAKING INTO ACCOUNT 2010-2015 DATASET

3.1. GENERAL TRENDS

Summary statistics for the three new (2010-2015) datasets, as listed in Section 1, are presented in **Tables 2**, **3** and **4**. Clear trends are apparent in the use of MTBE vs. ETBE in gasoline, and also in total GEO content, as follows:

- From 1999 to 2010 the dominant ether oxygenate in gasoline was MTBE, whereas from 2010-2015 it was ETBE. The MTBE concentration in gasoline decreased from an average of 5.39 m/m% for 1999-2009 to an average of 1.10-1.63 m/m% for 2010-2015. In parallel, the ETBE concentration in gasoline increased from an average of 0.91 m/m% for 1999-2009 to an average of 1.67-6.32 m/m% for 2010-2015. This represents a continuation of the trend mentioned in Concawe Report 4/12 towards reduced MTBE and increased ETBE use in gasoline.
- TAME concentrations in gasoline have not changed materially over time with an average 0.29 m/m% in 1999-2009 and an average of 0.01-0.38 m/m% in the added datasets. The maximum concentration of TAME was 11.22 m/m% for 1999-2009 vs 7.53 m/m% for 2010-2015, with both fuel samples originating from Finland.
- DIPE concentrations in gasoline were similar in the 1999-2009 and added datasets, with an average of <0.01 m/m% and a maximum reported concentration of 0.01m/m% for a sample collected in the UK. However, DIPE was only analysed in one of the three added datasets.
- TBA concentrations in gasoline was also similar, the average being 0.03 m/m% in 2000-2009 and ranging from 0.02-0.04 m/m% in the 2010-2015 datasets. However, TBA was only analysed in two of the three added datasets.

3.2. REGIONAL VARIATION

TAME continued as the dominant GEO in Finland, whereas in other countries higher concentrations of MTBE and ETBE were present. ETBE continued as the dominant GEO in France and Spain, with only minor amounts of MTBE. In Germany and Italy ETBE and MTBE were used at broadly similar concentrations and in the UK GEO concentrations gasoline were generally low, up to 2.5 m/m%, and mostly represented by MTBE.

Table 2: EO in gasoline, from summer 2010 to winter 2011/2012, in 6 European countries. Mean, medium and maximum reported concentrations (m/m%) from a SGS database.

	Ether Oxygenates				
	MTBE	**ETBE**	**TAME**	**DIPE**	**TBA**
Total number of sampling events (n)					
	55	55	55	55	55
Mean (average) concentration in all European gasoline samples from summer 2010 to winter 2011/2012 (m/m%)					
	1.23	6.32	0.01	<0.01	0.04
Median concentration in all European gasoline samples from summer 2010 to winter 2011/2012 (m/m%)					
	0.06	5.07	<0.01	<0.01	0.02
Maximum concentration observed in individual sampling rounds (m/m%)					
Concentration (m/m%)	5.75	16.40	0.27	0.01	0.20
Gasoline type	PULP	PULP	PULP	PUL	PULP
Period	Summer 2011	Winter 2011/2012	Summer 2011	Summer 2010	Summer 2010
Country	Germany	France	Italy	United Kingdom	Finland

Table 3: EO in gasoline, in 2010, in 17 European countries. Mean, medium and maximum reported concentrations (m/m%) from a Concawe database (2010 Fuel Survey).

	Ether Oxygenates				
	MTBE	**ETBE**	**TAME**	**DIPE**	**TBA**
Total number of sampling events (n)					
	100	100	100	ND	100
Mean (average) concentration in all European gasoline samples in 2010 (m/m%)					
	1.10	3.32	0.24	ND	0.02
Median concentration in all European gasoline samples in 2010 (m/m%)					
	0.28	0.78	0.05	ND	<0.01
Maximum concentration observed in individual sampling rounds (m/m%)					
Concentration (m/m%)	10.29	14.71	3.31	ND	0.15
Gasoline type	PUL*	PUL*	PUL*	ND	PUL*
Period	2010	2010	2010	ND	2010
Country	Italy	France	Finland	ND	France

* Analysis were made on the most common type in the market and did not specify which quality (PUL or PULP) it was. However, since PULP is not that common, the fuel type that was analysed is most likely PUL.
ND= No data

Table 4: EO in gasoline, in 2015, in 17 European countries. Mean, medium and maximum reported concentrations (m/m%) from a Concawe database (2015 Fuel Survey).

	Ether Oxygenates				
	MTBE	**ETBE**	**TAME**	**DIPE**	**TBA**
Total number of sampling events (n)					
	100	100	100	ND	ND
Mean (average) concentration in all European gasoline samples in 2015 (m/m%)					
	1.63	1.67	0.38	ND	ND
Median concentration in all European gasoline samples in 2015 (m/m%)					
	0.40	0.10	<0.01	ND	ND
Maximum concentration observed in individual sampling rounds (m/m%)					
Concentration (m/m%)	14.27	14.01	7.53	ND	ND
Gasoline type	PUL*	PUL*	PUL*	ND	ND
Period	2015	2015	2015	ND	ND
Country	Italy	Spain	Finland	ND	ND

* Analysis were made on the most common type in the market and did not specify which quality (PUL or PULP) it was. However, since PULP is not that common, the fuel type that was analysed is most likely PUL.
ND= No data

3.3. ANALYSIS OF 2010-2015 TRENDS IN GEO USE

2009-2015 saw significant legislative developments in the EU around biofuels, with targets set on biofuel use under the Renewable Energy Directive (2009/28/EC) and Indirect Land-Use Change Directive ((EU) 2015/1513). The effect of these changes on GEO and also EtOH content was assessed by reviewing gasoline GEO and EtOH content data from 2010 and 2015 (**Table 5**). Both dataset were comprised of 100 gasoline samples from 17 countries. The individual countries listed have the highest fuel consumption (i.e. France, Italy, Spain and United Kingdom; note that Germany was excluded since no data for 2015 was available). For EtOH additional SGS survey data from 2006-2009 is presented to show the pre-2010 baseline.

While a detailed analysis of factors influencing ether oxygenate and EtOH use in gasoline is beyond the scope of this study, the statistics presented in **Table 5** show a clear increase in gasoline EtOH content from 2006-2009 to 2010 and 2015, which is consistent with the drive for increased use of biofuels. In contrast the concentration of ETBE, which can be produced from bioethanol, declined from 2010 to 2015 while the concentration of MTBE either increased or (in the case of France where EtOH and ETBE are dominant) slightly decreased.

From a soil and groundwater risk management perspective, the 2010 and 2015 data indicate an overall decrease in total GEO content from 4.66 to 3.68 m/m%, and an increase in EtOH content (from 3.42 to 4.60 m/m%). The statistics for the individual countries are more complex: France and the UK follow the overall trend, however in Italy and Spain where EtOH content has only increased slightly there has been a small increase in total ether oxygenate content.

***Table 5**:* Summary of trend analyses for 2010 and 2015 data, all concentrations are in m/m%. For EtOH additional SGS survey data from 2006-2009 is presented to show the pre-2010 baseline. Addition of * means the change is significant using the t-test[1] with alpha = 0.10.

Mean (average) concentrations in gasoline samples											
	ETBE (m/m%)		MTBE (m/m%)		TAME (m/m%)		Sum ETBE, MTBE and TAME (m/m%)		EtOH (m/m%)		
	2010	2015	2010	2015	2010	2015	2010	2015	2006-2009	2010	2015
Whole dataset	3.32	1.67*	1.10	1.63	0.24	0.38	4.66	3.68*	0.79	3.42	4.60*
France	7.31	5.49	0.19	0.02*	0.24	0.02	7.73	5.52	0.91	6.33	7.72
Italy	1.80	0.09*	2.07	4.85	0.03	0.49	3.90	5.43	0.02	0.04	0.32
Spain	0.20	0.03*	11.49	12.69	0.06	<0.01*	11.76	12.72	0.35	1.20	1.82
UK	0.37	0.05*	0.08	0.07	0.07	<0.01	0.52	0.12*	0.53	2.15	5.00*

[1] The t-test can be used to determine if two sets of data are significantly different from each other. If the t-value is less than the chosen significance level (also denoted as alpha), the null hypothesis that there is no significant difference between the two datasets can be rejected and one may conclude that the effect reflects the characteristics of the whole dataset. For example, a significance level of 0.10 indicates a 10% risk of concluding that a difference exists when there is no actual difference.

4. CONCLUSIONS

Trend in fuel composition from averages based on 1999-2009 dataset (as reported in Concawe Report 4/12) vs new 2010-2015 averages

Prior to 2010 the average EtOH concentration in EU gasoline was 0.79 m/m%. Since then there has been a marked increase in the use of EtOH in gasoline formulation, with the average concentration increasing to 3.42 m/m% in 2010 and 4.60 m/m% in 2015.

While the average concentration of the sum of ETBE and MTBE in EU gasoline remained approximately constant between 1999-2009 and 2010-2015, there was a shift towards higher ETBE concentration (from 0.91 to 1.67-6.32 m/m%) and lower MTBE concentration (from 5.39 to 1.10-1.63 m/m%). Average DIPE and TBA concentrations remained low over the period 2010-2015 (average concentration <0.01 m/m% and reported maximum concentration decreasing from 0.88 m/m% to 0.01 m/m% in 2010). The use of TAME as a GEO continued in Finland but only minor concentrations were present elsewhere (average concentration <0.5 m/m%).

More recent trends in fuel composition (2010 and 2015 data)

Comparing 2010 and 2015 data indicates an overall decrease in the sum of ETBE and MTBE content from 4.66 to 3.68 m/m%, and an increase in EtOH content (from 3.42 to 4.60 m/m%). Over the same time period the average ETBE concentration decreased from 3.32 to 1.67 m/m%, which is contrary to the longer term (1999-2015) trend mentioned above and suggests that EtOH has to some extent replaced ETBE as the main biofuel component. The statistics for the individual countries are more complex: France and the UK follow the overall trend, however in Italy and Spain where EtOH content has only increased slightly there has been a small increase in total ether oxygenate content.

Soil and groundwater risk management considerations

The implications of the observed increase in EtOH with the concomitant decrease in ETBE, on fate and transport of GEO in soil and groundwater, raises three points for consideration in addition to those summarised in Concawe Report 4/12. These points can be summarised as follows:

1. A decrease in the EO content of gasoline would, for any given spill, reduce the mass of EO introduced to the subsurface and the extent of any groundwater EO plume (where applicable)

2. The high biodegradability of EtOH under aerobic and anaerobic conditions (Firth et al., 2014; Powers et al., 2001), would mean that a small increase in gasoline EtOH concentration would not have any material effect on the impact to groundwater. Field investigations have confirmed the low migration potential of EtOH, for example in a controlled small-volume release of E10 (10% EtOH and 90% conventional gasoline) (Feris et al., 2008; Mackay et al., 2006) it was found that EtOH was detected in groundwater rarely and only at one location 0.5 m downgradient of the injection wells.

3. At higher EtOH concentrations there is the potential for anaerobic biodegradation of EtOH to methane gas (Powers et al., 2001), which should be taken into account as part of the risk assessment in the event of a spill.

5. GLOSSARY

DIPE	Di-isopropyl ether
ETBE	Ethyl tertiary butyl ether
EtOH	Ethanol
EO	Ether oxygenate
GEO	Gasoline ether oxygenate
MTBE	Methyl tertiary butyl ether
PUL	Premium unleaded (gasoline)
PULP	Premium unleaded plus (gasoline)
SGS	Société Générale de Surveillance
TAME	Tertiary amyl methyl ether
TBA	Tertiary butyl alcohol
THxEE	Tertiary hexyl ethyl ether

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