

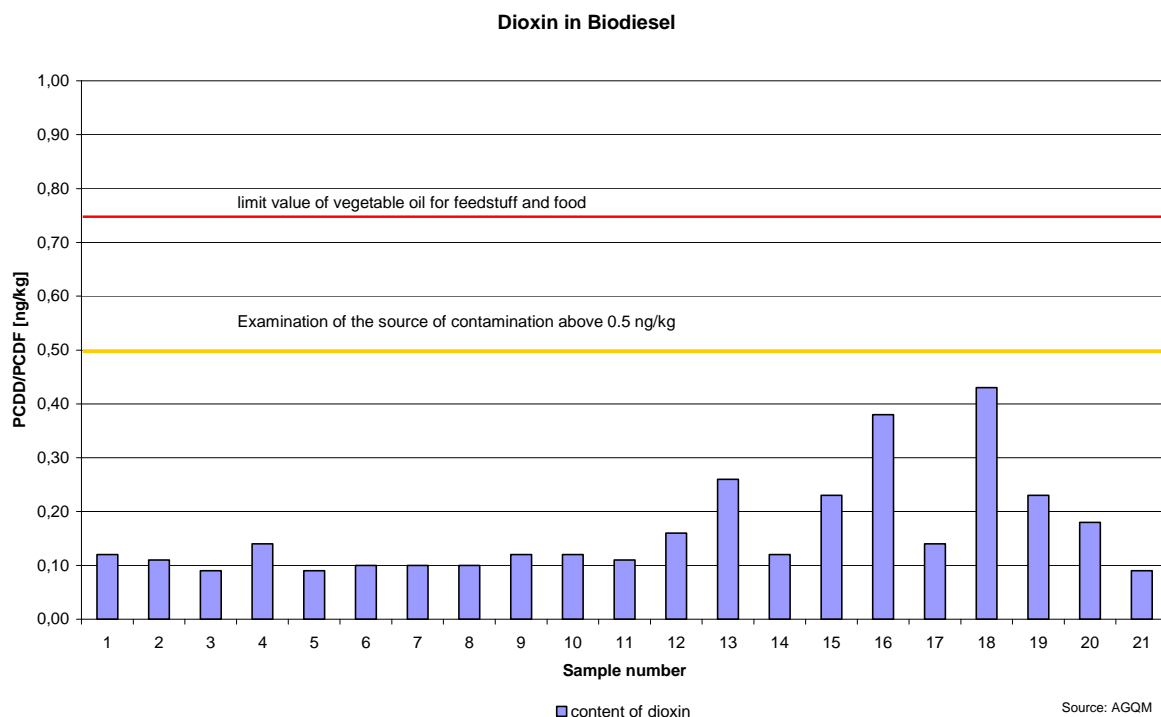
Analysis of biodiesel for dioxin content

Background

The reason for measuring the dioxin concentration in biodiesel was the scandal concerning dioxin-contaminated animal feed at the end of 2010. Fatty acids from biodiesel production only intended for technical use and accordingly labelled correctly had been used in animal feed. It was shown with absolute certainty that the cause of the dioxin was not the fatty acids; still, dioxins were seen in relation with biodiesel by the public at large. For this reason, AGQM initiated a corresponding analysis of Biodiesel.

Results

A total of 21 samples was obtained from biodiesel producers, most of which came from an unannounced sampling campaign by an independent testing institution. The analytical work was carried out by an accredited laboratory in March 2011.



PCDD/PCDF: Polychlorinated dibenzodioxins and polychlorinated dibenzofurans

The graph above illustrates the dioxin content of 21 different biodiesel samples in units of ng^a/kg. In most cases the values are below the quantification limit. Below the quantification limit of the method no exact result can be determined. In case the measured value is below the quantification limit, the limit value is reported as dioxin content.

The „dioxin content“ is indicated as the sum of the different congeners of polychlorinated dibenzodioxins and dibenzofurans. Congeners can be traced back to the same parent compound (e.g., dibenzodioxin) whereas they differ, e.g., in the number of chlorine atoms.

^a ng: Nanogram; 1 ng = 0,000000001 g = 10⁻⁹ g



According to a World Health Organization (WHO) directive, factors are assigned to the different congeners reflecting the level of toxicity (TEF, toxicity equivalence factors). This means that critical congeners are weighted more heavily in the sum than less critical congeners. If the value of a congener is below the level of quantification, the level of quantification is considered for the calculation of the sum total. The level of quantification of different parameters can vary within certain limits due to the presence of interfering signals. The sum total of all components illustrated in the diagram is decisive for the limit value.

As technical product, biodiesel must meet the limits defined in the ‘Chemikalien-Verbotsverordnung’ (regulation prohibiting the use of certain chemicals), which are of the order of $\mu\text{g}^b/\text{kg}$. To compare the dioxin contents measured in biodiesel with limits for animal feed and foodstuffs, reference is made to the limits for vegetable oils defined for animal feed in the Commission Regulation 2006/13/EC and for foodstuff in Commission Regulation 1881/2006. They are the same for animal feed and foodstuffs even if indicated in different units, i.e., 0.75 ng/kg and $0.75 \text{ pg}^c/\text{g}$, resp., which means they are lower by several orders of magnitude than for technical products.

Discussion of the congener pattern

In 14 of 21 samples the values for all congeners were below the limit of quantification. In these cases no interpretation of the congener pattern is possible. The sum total of all components is calculated by addition of the limits of quantification as described above.

In 7 samples up to five congeners could be quantified: two samples with one congener, one sample with two congeners, one sample with three congeners, two samples with four congeners and one sample with five congeners above the limit of quantification. In all samples octachlorodibenzo-p-dioxin (OCDD) was found which contributes only marginally to the sum total due to the low TEF factor. The distribution of the congeners is summarised in the table below.

amount congeners	amount samples	OCDD	HpCDD	HxCDD	HpCDF
1	2	x	-	-	-
2	1	x	x	-	-
3	1	x	x	-	x
4	2	x	x	x	-
5	1	x	x	x	x

x: above limit of quantification; -: below limit of quantification

The tetra and pentachlorinated dioxins which are of high toxicological concern were below the limit of quantification in all samples.

Summary and conclusion

AGQM had analysed a total of 21 different biodiesel samples for dioxins by an accredited laboratory. The dioxin contents in all samples were below the level permitted for foodstuff or animal feed and therefore lower by far than the limits defined for technical products, in most cases even below the quantification limit of the analytical method.

^b μg : Microgram; $1 \mu\text{g} = 0,000001 \text{ g} = 10^{-6} \text{ g}$

^c pg : Picogram; $1 \text{ pg} = 0,000000000001 \text{ g} = 10^{-12} \text{ g}$



In the German Federal Environment Agency's publication "Dioxine und dl-PCB in der Umwelt" (March 2010) the reports of the German Federal States regarding the environmental impact of dioxins are summarised and evaluated. The report takes account of data referring to samples of soil, feed and food. The content of dioxins and furans is dominated by octa- and heptachlorinated congeners. The analysis of all data shows that the "typical" German congener pattern complies with the congener pattern of the analysed Biodiesel samples. The determined dioxins can be explained by the common environmental impact in Germany.

These results provide impressive proof that dioxins in biodiesel are no reason for concern because they not only comply with the requirements concerning the dioxin content in technical products but also with the even more stringent limits defined for animal feed and foodstuff.