

## Newsletter

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### Content:

1. ADI Values and Drinking Water Guide Values for Active Agents in Pesticides
2. Perfluorocarbon Compounds (PFCs) in the Environment
3. BfR Glyphosate Analysis Appears Not to Lead to a Reevaluation of Health Risk
4. Visit us at the Food Safety Kongress in Berlin

### ADI Values and Drinking Water Guide Values for Active Agents in Pesticides

by Dr. Sven Steinhauer, Carsten Schaffors, GBA Laboratory Group

When pesticides are utilized, their active agents inevitably reach the environment. Depending on the way they are applied, they can be detected in soil, bodies of water, and food products. Special authorization processes in the European Union have been designed to ensure two factors: the effectiveness of pesticides and the prevention of detrimental effects on the consumer, the environment, or third parties. Potential hazards to the health of consumers caused by residual amounts of pesticides in food products and drinking water should be eliminated under any circumstances.

For this purpose, the authorization and usage of pesticides has been regulated in Germany since 1968. In the European Union, the active substances in pesticides have been assessed by a community procedure according to the guideline 91/414/EWG since the 1990s. On June 14<sup>th</sup>, 2011, this guideline was supplanted by the EU directive 1107/2009.

The German Federal Institute for Risk Assessment (*Bundesinstitut für Risikobewertung / BfR*) participates in this process by conducting health tests derived from the ADI values (Acceptable Daily Intake) provided by the World Health Organization (WHO).<sup>[1]</sup> The ADI value is the amount of an active substance per kg of body mass that a person can consume on a daily basis over the course of a lifetime without health risks. They are based on results from comprehensive toxicological studies derived from international conventions. Based on the ADI values, the BfR calculates the drinking water guide values ( $LW_{tw}$ ) for the active agents in pesticides that are allowed in Germany. These are valid for a person with an average body mass of 70 kg and a daily water consumption of two liters, thereby exhausting only one tenth of the ADI value.

For the example of glyphosate, which has an ADI value of 0.3 mg/kg, the drinking water guide value is 1,000 µg/L and thus the highest allowed value for an active substance, because a cap (upper limit) has been set at 1,000 µg/L for all active substances.<sup>[1]</sup>



The drinking water guide value ( $LW_{TW}$ -Value), which is theoretically derived, is not to be confused with the limit values defined by the drinking water ordinance, which generally are several factors smaller than these health limit values and are legally binding.

Using the process described above, health limit-concentrations have also been set for substances other than the active agents in pesticides (such as biocides and metabolites). If these limit values for active agents in pesticides or biocides are exceeded, then the guide values ( $LW_{TW}$ ) can help the German environmental agency (*Umweltbundesamt*) to define what is a tolerable divergence according to the "action values" ( $MW_{TW}$ ). These are considered safe for one's health and temporarily tolerable (up to a maximum of three years).

A complete table comparing the ADI values with the guide values and action values can be found in the full article published by the Federal Institute for Risk Assessment (BfG) at the following link: <http://www.bfr.bund.de/cm/343/pflanzenschutzmittel-wirkstoffe-adi-werte-und-gesundheitliche-trinkwasser-leitwerte.pdf>.

Analyzing the various active agents in the field of pesticides and their metabolites is one of the GBA Laboratory Group's core competencies. Changes in the usage and authorization of pesticides is therefore a topic which the GBA Laboratory Group monitors continuously. The increasing detection requirements in a wide variety of matrices with continuously lowered limits of quantification demand a comprehensive technical expertise. If you have any questions about pesticides and their metabolites, we will gladly assist you.

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Literature:

<sup>[1]</sup> Aktualisierte Information Nr. 030/2013 des BfR , 03 December 2013

<sup>[2]</sup> Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz, 2003, 46, 701–706 & 2003, 46, 707–710

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## Perfluorocarbon Compounds (PFCs) in the Environment

By Carsten Schaffors, GBA Laboratory Group

In the year 1949, the company "3M" began the production of perfluorocarbon compounds (PFCs) by introducing the electrochemical fluorination process. During this relatively untargeted production process, a mix of branched and unbranched fluorinated carbon chains with a length of about four to nine carbon atoms are initially formed. Due to the unique chemical-physical properties (chemical stability, surface tension, hydrophobic, lipophobic, and dirt-repellant) of the material groups developed in this way, the number of applications increased from 1966 until the 1990s in a wide variety of products. PFCs were utilized in inks, paints, waxes, lubricants, hydraulic fluids, coatings for leather, paper, and textiles, fire extinguisher foam, for galvanizing and cleaning metal surfaces, in the semiconductor industry, as well as in photography and photolithography. In the year 2000, when the company 3M announced their exit for 2002 from the production of POSF (perfluorooctanesulfonyl fluoride,  $C_8F_{17}SO_2F$ -Group), they accounted for almost 80% of the worldwide production of 4,650 tons of POSF. This was the most important intermediary product in the production of a wide variety of PFCs, including perfluoroalkyl carbon acids (PFCAs) and perfluoroalkyl sulfonates (PFASs). The biggest production sites were located in Decatur, Alabama, USA and Antwerp, Belgium. The U.S. EPA identified 20 additional companies outside of the USA that produced POSF.<sup>[1]</sup>



The worldwide production of POSF between the years 1970 and 2002 is estimated at approximately 96,000 t (122,500 t including the unusable waste). In the period between 1970 and 2012, it is assumed that over 42,250 t of contamination have reached the air and waterways, leading to ubiquitous distribution in the environment. POSF production and its usage in various consumer goods are thus directly responsible for the contamination.<sup>[1]</sup> High concentrations of perfluoric acids (PFAs include both perfluoroalkyl carbon acids, PFCAs, and perfluoroalkyl sulfonates, PFASs) in rivers near industrial production sites as well as in the outlet pipes of sewage treatment plants support this hypothesis.<sup>[2]</sup> It is estimated that about 450 to 2,700 t of PFOS (perfluorooctane sulfonate) have reached the sewage lines by washing treated carpets and clothes as well as from fire extinguisher foam.<sup>[1],[3]</sup> Preliminary and intermediate products (e.g. fluorotelomer sulfonates and perfluoroalkyl sulfonamides) during the production process as well as impurities in the production process of PFOS account for the amount of indirect contamination. The atmospheric PFC contamination in the environment is caused by the volatile preliminary and intermediate products and their oxidization, urban atmospheres, and volatile components in consumer products.<sup>[2],[3]</sup> Current estimates of PFOS in the world's oceans range from 235 to 1,770 t.<sup>[1]</sup>

Since these groups of substances are now found everywhere, even in Arctic and Antarctic ice, PFOS was defined as a "PBT-Substance" (persistent, bioaccumulative, and toxic) at the 2009 Stockholm-Convention and added to the list of POPs (persistent organic pollutants). In 2008, the usage of PFOS was banned in the EU when the directive 2006/122/EC went into effect. In 2010, the OSPAR commission ([www.ospar.org](http://www.ospar.org)) published a list of 17 PFCs that met the following criteria for inclusion: posing a threat to the aquatic environment and the marine environment, widespread distribution in one or more habitat in the oceans, as well as a danger to human beings due to potential absorption through the food chain.<sup>[4]</sup>

PFCs with chain lengths of more than eight carbon atoms are accumulated in the food chain and thus also lead to elevated concentrations even in more complex organisms. The PFOS content in human blood reached a plateau at the end of the 1980s. The discontinuation of PFOS production should, in fact, lead to a decline in these values. Studies in the USA and Europe have provided evidence of this decline since 2001, in China since 2004. In Japan, no significant reductions in concentrations have been measured.<sup>[4]</sup>

The ubiquity of PFAs in a wide variety of environmental matrices is illustrated here in data from a study from the USA.<sup>[2]</sup>

8.28–16.0 pg/m <sup>3</sup>	Air
0.91–13.2 ng/L	Rainwater
0.91–23.9 ng/L	Snow
1.11–81.8 ng/L	Surface runoff
9.49–35.9 ng/L	Lake water

Investigations in the Rhein river from almost 70 different measurement points resulted in a total PFAS content between 4 and 620 ng/L.<sup>[5]</sup> PFBS (perfluorobutane sulfonate) and PFBA (perfluorobutane acid) dominated in this case, accounting for up to 94% of the findings. These short-chain PFCs, among others, have replaced the usage of PFOS and PFOA (perfluorooctane acid). However, the PFOS content was still recorded at 0.89 to 24.8 ng/L and the PFOA concentration between 0.61 and 42.1 ng/L.<sup>[5]</sup>

With the revisions to the earlier guidelines, 2000/60/EC and 2008/105/EC, and with the guideline 2013/39/EU taking effect on August 12<sup>th</sup> 2013, the environmental quality norms for a variety of priority substances, including PFOS, were newly determined in the context of the implementation of the European Water Framework Directive (WFD). (For more information, also see issue 4 of the GBA Newsletter from December 2013, which can be found on our homepage at: <http://www.gba-labor.de/en/newsletter-archive.html>.)

The environmental quality norm of 0.65 ng/L for PFOS in surface water, which was set by the EU, may seem ambitious considering the ubiquitous distribution of PFOS (the detection limit given in the method DIN 38407-F42 is 10 ng/L), especially when it remains unclear how much of the widespread contamination is a result of indirect emissions. For example, it has not yet been investigated whether the rise in PFOS and PFOA concentrations found in the outlet pipes of sewage treatment plants may be caused by biological decomposition of fluorotelomer sulfonates or fluorotelomer alcohols.

If you have any questions concerning this topic or others, we will gladly assist you.

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#### Literature:

- [1] „A first global production, emission, and environmental inventory for perfluorooctane sulfonate“, Alexander G. Paul, Kevin C. Jones, Andrew J. Sweetman, Environmental Science & Technology 2009, 43, pp. 386-392, 03 November 2008
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- [3] „Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSS)“, Michio Murakami, Hiroyuki Shinohara, Hideshige Takada, Chemosphere 74 (2009), pp. 487-493, 05 October 2008
- [4] „Trends of polyfluoroalkyl compounds in marine biota and in humans“, Renate Sturm, Lutz Ahrens, Environmental Chemistry 2010, 7, pp. 457-484, 05. October 2008
- [5] „Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed“, Axel Möller, Lutz Ahrens, Renate Sturm, Joke Westerveld, Frans van der Wielen, Ralf Ebinghaus, Pim de Voogt, Environmental Pollution 158 (2010), pp. 3243-3250, 14 Juli 2010

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## BfR Glyphosate Analysis Appears Not to Lead to a Reevaluation of Health Risk

By Dr. Sven Steinhauer, Carsten Schaffors, GBA Laboratory Group

Glyphosate (N-(Phosphonomethyl)glycine) is the most commonly used active agent in herbicides worldwide. It is utilized in agriculture and horticulture in order to combat weeds. The agent is deployed before sowing and destroys a plant-specific enzyme in weeds that is responsible for the creation of special amino acids. Outside of the European Union, the agent can also be applied after sowing the seeds of plants that have been genetically altered to exhibit glyphosate resistance. Glyphosate also serves as a ripening agent, which can be applied in order to enable uniform ripening and an earlier harvest.<sup>[1]</sup>

In recent years, due to the large number of studies published and the wide range of assessments, a controversy has arisen concerning the health risks of the herbicidal agent glyphosate. Every active agent in pesticides and herbicides is regularly examined for further approval in the context of the routine EU testing procedures. That allows state-of-the-art technology and the latest research results to be taken into consideration before issuing or extending authorization. For the active agent glyphosate, Germany is responsible for generating the reports for the other EU member states.



For the report on the health risks, the BfR (German Institute for Risk Assessment) checked and evaluated 150 additional new toxicological original studies and over 1000 studies newly published in scientific journals.<sup>[2]</sup> After this analysis, the BfR has come to the conclusion that neither the health limit value nor the ADI value (acceptable daily intake) must be altered significantly. In animal testing, there was no indication of carcinogenic effects or negative effects on reproduction and fertility due to glyphosate.<sup>[3]</sup> The active agent does not accumulate in the human body and is listed neither as a PBT-substance (persistent, bioaccumulative, and toxic) nor as a persistent organic pollutant (POP). The risk of groundwater contamination is minor.<sup>[2]</sup> It is more likely that an additive contained within the pesticide or herbicide (e.g. a wetting agent) may potentially demonstrate higher toxicity levels than the active agent itself.<sup>[4]</sup>



Glyphosate belongs to the group called "substitution candidates." It fulfills the approval requirements of the EU ordinance, but in some aspects it compares less favorably than other agents. For this reason, it should be replaced by other active agents if possible.<sup>[2]</sup> The secondary effects of widespread herbicides like glyphosate are cause for additional concern. It is not directly harmful to birds, mammals, and insects, but by eliminating wild herbs on the cultivated area, both insects (e.g. butterflies and wild bees) and thus also the associated types of birds, such as partridges and skylarks are deprived of their source of food.<sup>[2]</sup>

The BfR report has been made available to the EU member states for their comments and will be revised after taking all of the incoming comments into consideration. Subsequently, a total evaluation of glyphosate is expected to be created and published by the European Food Safety Authority (EFSA) at the end of 2014. After that, the commission will make a decision concerning the further authorization of the active agent glyphosate based on the German evaluation report and taking into consideration all of the comments received.<sup>[2]</sup>

Further information can be found on the BfR homepage (<http://www.bfr.bund.de/en/home.html>) and the EFSA homepage (<http://www.efsa.europa.eu>).

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Literature:

<sup>[1]</sup> „Fragen und Antworten zur gesundheitlichen Bewertung von Glyphosat“, Updated FAQ from the BfR, January 15th, 2014

<sup>[2]</sup> „EU-Bewertung von Glyphosat geht in die nächste Phase“, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, Newsletter Nr. 1, updated January 7th, 2014

<sup>[3]</sup> „Das BfR hat einen Entwurf zur Neubewertung des gesundheitlichen Risikos von Glyphosat erstellt“, Homepage des Bundesinstituts für Risikobewertung, updated December 5th, 2013

<sup>[4]</sup> „Glyphosat: Nicht giftiger als bisher angenommen, aber bestimmte Beistoffe sind kritisch zu betrachten“, BfR Press Release 03/2014, January 20th, 2014

## Visit us at the Food Safety Kongress in Berlin

On March 11<sup>th</sup> and 12<sup>th</sup> 2014, the 6<sup>th</sup> Food Safety Congress will take place at the Ellington Hotel in Berlin. With the motto "Trust in Food Products – From the Producer to the Consumer," there will be numerous presentations by renowned speakers from the political and economic fields, as well as an interesting array of workshops dealing with the topic of safety and protection in the food industry.

The GBA Laboratory Group will be represented with an informational booth on site. Here you will have the opportunity to get to know our analytical services better. Furthermore, at 6:15 p.m. on the first day of the convention, Dr. Sven Steinhauer, Director of Research & Development at GBA, will be holding a presentation on the topic of "Drinking Water in the Food Production Industry." The presentation will deal with the following issues:

- Developments in food law concerning drinking water
- Laws, ordinances, and certification
- Public Health Department requirements
- Biofilm bonding and microbial contamination – where are the usual suspects?
- Prevention and monitoring – for whom? how often? by whom?

The Food Safety Congress has established itself as a central meeting point for companies in the field. Contact us in order to receive a 15 % discount on your participation in the Food Safety Congress 2014 with the GBA Laboratory Group.

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