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Derivation of insignificant threshold values for the ground water

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1 Task and problem

For the national evaluation of changes in the groundwater quality that have already occurred or that are to be prevented, transparent and uniform evaluation criteria are necessary. This includes in particular a scale for classifying anthropogenic and regionally limited changes in the chemical aroundwater insignificant quality of the as or vet detrimental. The Bund-/Länderarbeitsgemeinschaft Wasser (LAWA) considers the insignifiant threshold values (short: GFS) to be a suitable scale for this purpose.

In 2004 and with the approval of the Conference of Environmental Ministers, the Bund-/Länderarbeitsgemeinschaft Wasser (LAWA) published the "Derivation of insignificant threshold values for the ground water" report. The report comprises the concept for the derivation of the insignificant threshold values, application principles and substance data sheets. The latter comprise the reasons for the derived insignificant threshold values. The values are ecotoxicologically and human toxicologically based (particularly according to the requirements of the Drinking Water Ordinance).

Legal changes by EU and federal government as well as new scientific findings since the publication in 2004 cause the necessity of a verification of the values. Mainly as a consequence of coming into effect of Directive 2008/105/EC, which defines environmental quality standards (EQS) for priority substances and certain other pollutants for surface water bodies, the values need to be updated. On its 61st meeting on 8/9 June 2010, the LAWA-AG therefore decided under TOP 5.2 to set up an ad-hoc subcommittee "Updating the data sheets of the insignificant threshold values (short title: GFS updating)". On its 140th meeting, the LAWA plenary assembly agreed. The subcommittee's task comprised the verification of the substance lists, the determination of need for change due to a) Directive 2008/150/EC, b) the Surface Waters Ordinance and c) new (eco-) toxicologic findings as well as the update of the data sheets of the LAWA publication "Derivation of insignificant threshold values for the ground water" resulting from these steps. The present report "Derivation of insignificant threshold values for the groundwater" is based on the criteria of 2004 that have been developed further for this update.

The advanced water legislation made it necessary to adjust the terms used in the 2004 report to those of the new WHG (2009) and also extended the scope *(thresholds according to GrwV/EU-Grw-RL)*.

Within the scope of an adhoc-sub-committee working group, the Bund-/Länderarbeitsgemeinschaften Wasser (LAWA), Abfall (LAGA) and Bodenschutz (LABO) have worked out principles for the application of the insignificant threshold values in the different legal areas (chap. 3).

2 Derivation of insignificant threshold values

2.1 Principles and concept

The insignificant threshold values (GFS) is defined as concentration at which despite an increase in the substance contents as compared to regional background values, no relevant ecotoxic effects can occur and the requirements of the Drinking Water Ordinance or correspondingly derived values can be complied with.

This is to ensure that the groundwater

- > remains usable everywhere for human use as drinking water and
- is maintained intact as habitat, amongst others as groundwater is part of the ecosystem and constitutes the base flow into surface water or influences the character of groundwater-dependent terrestrial ecosystems.

For the derivation of the GFS values, one primarily uses broadly agreed human and ecotoxicological data. That means that legally controlled values are regarded as having been defined and thus take priority over values on the basis of an expert evaluation. Apart from that, publications of individual test results are usually not used but substance valuations discussed and accepted in the professional public, particularly on EU level.

If different values are derived in the derivation with regard to the drinkability and with regard to ecotoxicological criteria, the insignificant threshold value will correspond to the lower value. If only ecotoxicological data is available, a plausibility check by means of the GOW concept (see chap. 2.2.3) will be carried out with regard to the human toxicological effect. If only human toxicological data is available, a plausibility check with regard to the ecotoxicological effect will be carried out in the individual case, as no systematic test concept has been developed for this constellation, yet.

The protection of "fish eating" animal species as well as human health due to the consumption of fish is not considered in the definition of the values as these aspects are not relevant for the groundwater. This explains why stricter requirements are made on the environmental quality standard (EQS) for Biota and its corresponding concentrations in the surface water for mercury, hexachlorobenzene and hexachlorobutadiene than on the groundwater.

As in individual cases, the derived values may be within very low concentration ranges, a minimum limit of 0.01 μ g/l was defined in a subsequent step unless legally binding values, Europe-wide agreed PNECaquat. (= predicted no effect concentration) or values are concerned, for which an affect has been proven.

2.2 Methodology for individual substances

2.2.1 Evaluation based on the Drinking Water Ordinance

Water in which limit values of the Drinking Water Ordinance (TrinkwV, 2001) are exceeded may - according to § 9 TrinkwV - only be put into circulation as drinking water under strict conditions and not permanently. As far as the values specified there either correspond to the justification option "Harmless to human health" or the option "Aesthetically unobjectionable quality of the drinking water", i.e. which are neither caused by preparation nor distribution reasons, they will be accepted with priority and without changes when determining the insignificant threshold values.

If the limit values of the Drinking Water Ordinance have preparation- or distribution-related reasons or if limit values for relevant parameters are missing, a health and aesthetic evaluation will be carried out in the individual case analogously to TrinkwV. The own human toxicological derivations that have been completed are primarily based on the toxicological basic data (Eikmann et al., 1999). If no information is available there, one falls back on toxicological substance data as they have been used in the calculation of test values for the evaluation of legacy (UBA, 1999). Apart from that, other suitable references such as the substance reports of WHO (2012) or the Integrated Risk Information System (IRIS 2012) or U.S. EPA are used. In the case of own human toxicological derivations, the individually evaluated references are directly specified in the justifications in the substance data sheets.

The proportionate utilization of the tolerable body dose via the drinking water path was usually set to 10% (Schellschmidt und Dieter, 2000). In this connection, it is assumed that substances are mainly taken in via food and not via drinking water. For substances common in drinking water and for substances that are naturally available in the overall drinking water system, assignment quotas of up to 100% may be acceptable. For the calculation of a tolerable concentration of non-carcinogenic substances in water, a daily intake of 2 litres of water and a body mass of 70 kg has been taken as basis. For carcinogens, one generally uses cancer risk evaluations after oral intake which have been assessed as qualitatively suitable. In compliance with the Drinking Water Ordinance (Directive 98/83/EC),

an additional lifetime risk of 1.10⁻⁶ was assumed as risk level for the carcinogenic substances.

If only risk projections are available which - based on certain quality criteria (Kalberlah et al., 1999) - UBA has assessed to be scientifically not reliable, you can also make alternative calculations to derive the GFS. These calculations can be carried out according to the benchmark procedure of U.S. EPA, with the lower 5% confidence range of the 10% benchmark response as starting point (quality criteria for curve adjustment: usually at least the data regarding the control group and three dose groups, model fit: p > 0.1, chi-square within -2 to +2, BMD/BMDL ratio < 10), or, if this is not possible, according to the EU T25 concept (Sanner et al., 2001; Dybing et al., 1997). As widely agreed method, the T25 concept insofar replaces the previous concept accordingly provided for the derivation of GFS of the carcinogenic effect level CEL_{min} ("minimal carcinogenic effect level"; Konietzka, 1999) in 10% of the collective. In general, comparable results can be expected with both methods.

From the relevant starting point, there is a linear extrapolation to the calculative additional lifetime risk of $1 \cdot 10^{-6}$ and the result is used in the GFS calculation as tolerable body dose for life from the health point of view. Due to the increased sensitivity of children to genotoxic carcinogens, an additional safety factor of 5.87 will be considered for these substances with scientifically reliable risk projections covering the entire average life expectancy of 70 years (Dieter und Henseling, 2003) unless the human toxicologically justified value for such substance (benzene, benzo(a)pyrene and vinyl chloride) was directly taken from TrinkwV.

The aesthetic evaluation analogously to TrinkwV considers parameters such as taste, smell, colour and turbidity of the water. For the justification of GFS values, the smell has previously been paramount. However, it is not the lowest smell threshold described that is decisive for an evaluation of the sensory perceptibility. Based on the US American SMCL values ("secondary maximum contaminant level"; US EPA, 1996; Stocking et al., 2001) which are supposed to prevent a considerable number of persons from stopping to use drinking water provided for the public for aesthetic reasons, the threshold values are defined to a maximum of the 30th percentile of the sensitivity distribution. At such value, the large majority of the population (70%) does not have any sensory perception.

In mixtures of contaminants with disturbing smell, the individual components are added up. In this connection, the synergism of neutral smell components, found by Rosen et al. (1963), is not taken into consideration, because a supra-additive effect of the individual components described by one of these authors cannot be quantitatively recorded due to missing data.

2.2.2 Evaluation with regard to ecotoxic effects

For the derivation of insignificant threshold values, one falls back to ecotoxic data from tests with surface water organisms. This is appropriate as:

- There are no standardised test procedures with groundwater organisms and
- It can be assumed that the biocoenosis of the groundwater is represented by the sensitivity spectrum of the organisms in surface water bodies in a first approximation.

A research project of the Federal Environment Agency (UBA, 2001) showed that ecotoxicological effects of the plant protection agents considered in the project occur in ground and surface water species in concentrations of comparable sizes. The harmful effect on the groundwater organisms, however, last considerably longer (or even have to be considered to be irreversible). This is not considered in the acceptance of ecotoxicological data of the standard organisations for the derivation of the insignificant threshold values.

Apart from that, surface water bodies are fed by the groundwater. Consequently, their quality requirements can usually also be used for the groundwater. This is also confirmed by the Water Framework Directive (WFD (2000/60/EC)). Annex V no. 2.3.2 WFD specifies that "the chemical composition of the groundwater ... have to be designed so that the concentrations of pollutants are not as high as would result in failure to achieve the environmental objectives specified under Article 4 for associated surface water bodies."

In 2004, environmental quality standards were considered with priority and without changes for the evaluation of the ecotoxicological effect and they were then used with decreasing priority PNE_{Caquat} , LAWA targets for the protection of the aquatic biocoenosis and MPA values (Maximum Permissible Addition). As the LAWA targets have been replaced by the EQS of the Surface Water Bodies Ordinance (OGewV, 2011) and the MPA approach is in the meantime rejected all over the EU, ecotoxicological data in the following order are considered for updating the derivation of the insignificant threshold values:

1. Legally binding, ecotoxicologically justified environmental quality standards (EQSs) for aquatic biocoenoses of the surface water bodies will be considered with priority when determining the GFS as in 2004.

In the GFS report 2004, the term Environmental Quality Standards comprised quality targets of the LAWA sample ordinance for implementation of Directive 76/464/EEC and its daughter directives and the EQS of Annexes 4 and 5 of the LAWA sample ordinance for implementation of Annexes II and V of the WFD. These environmental quality standards which were implemented in 16 national ordinances in 2004 have been laid down by law in the OGewV as national EQSs since 2011. EQSs that have already been revised (2013/39/EU) shall be implemented by September 2015.

If the definition of an EQS is not based on ecotoxicological but e.g. human toxicologically justified values, the ecotoxicology value proposed by the EU will be used.

- 2. The values for the "Predicted No Effect Concentration" (PNEC) from the Risk Assessment Reports (RAR) within the scope of Regulation (EEC) no. 793/93 on the evaluation and control of the risks of existing substances as well as PNEC values on the basis of Directive 98/8/EU for biocides rank second after the EQSs laid down in law. The PNEC values have been derived according to transparent principles uniform everywhere in the EU (Technical Guidance Document TGD 2003), have been checked by a large number of experts according to the regulations of the European Chemicals Legislation and have also been accepted upon availability of the RAR final report. Since 2004, RAR have been updated and more RAR have been published. Within the scope of the works regarding REACH, the TGD was replaced in 2003 by new guidance documents (e.g. ECHA 2008; TGD-EQS 2011 (EU, 2011)).
- 3. If there is neither an EQS nor a PNEC value according to no. 2 for a substance, proposals for EQS can be used if they have been proposed according to Lepper (2005) and in the future according to TGD-EQS (2011) by Member States of the European Union or accepted institutions (e.g. IKSR, RIVM) for the protection of the aquatic biocoenoses. Otherwise, substance evaluations discussed and accepted in the professional public, particularly on an EU level will be considered as in 2004.

In the following, the basic principles for the derivation of EQS, PNEC values and <u>quality criteria for</u> the protection of the aquatic biocoenoses are shown in the form of a summary. One aims at determining the concentration that does not pose a sustainable risk for an aquatic ecosystem.

The results from urgent and longer-term mono species tests at representatives of three different trophic levels (primary producers, primary consumers and secondary consumers) usually form the basis for the value derivation: Algae, invertebrates and fish. The test results allow for a statement or extrapolation regarding the relevant highest concentration which will have no effect, even in case of longer exposition (**No Observed Effect Concentration – NOEC**). The PNEC results from the lowest test result (for the most sensitive species) divided by a

compensation factor². This factor varies between 10 and 1,000, depending on the available data. By means of this factor, the uncertainties of the transfer of individual laboratory results at few organism species to real conditions in water bodies are to be considered. The principles defined in the TGD (2003) were used for the development of EQS according to WFD (Lepper, 2005) and adjusted to the scientific state-of-the-art in the TGD-EQS (2011) guidance document. In addition to the use of fixedly defined compensation factors, statistic procedures based on the distribution of the sensitivity of the species (SSD method: "species sensitivity distribution") are also admissible if there is a good data basis (at least 10 NOEC values from different species groups). Adjusted to the data basis, experts may in these cases consider compensation factors between 2 and 5.

In the risk evaluation of trace elements, particularly metals, it has to be considered that they are contained in the groundwater geogenically and that the organisms are naturally exposed to these usually low concentrations. The trace element concentrations naturally available in the aquatic environment are subject to temporal dynamics and may vary by several orders of magnitude. Within this overall range, organisms keep their intracellular level largely constant. For consideration of the geogenic background, so-called basic values were determined in 2004 by order of LAWA from the groundwater examinations compiled by the competent 16 state authorities. They were calculated for inorganic trace elements and fluoride as area-weighted mean of the

90th percentile values of 15 hydrogeological reference areas (Kunkel et al., 2004 with summary of the sands of the North German Plain in one reference area). The "non-representative" basic values for the parameters molybdenum, thallium and vanadium in 2004 have been confirmed as representative by the LAWA groundwater and water supply committee (LAWA AG) for molybdenum (Mo, 2012) and vanadium (V, 2008) due to ground water data systematically collected by the competent state authorities. For thallium, LAWA AG 2014 (TI, 2014) defined a basic value of < 0.1 μ g/l, due to the current surveys by the states. In 2012/2013, the entire data inventory of the competent state authorities was re-evaluated by the State Geologic Services (Wagner et al., 2014). These newly determined basic values were taken over for the derivation of the GFS values.

For the GFS value derivation 2004, the basic value was considered additively every time the total of ecotoxicological derived value and basic value was lower than the health-aesthetically derived value. According to TGD-EQS 2011, this procedure referred to as added-risk-approach (ARA) is not admissible. Consequently, the procedure has been changed to the effect that the basic value now replaces the ecotoxicologically derived value if the latter is lower than the basic value (total-risk-approach according to TGD EQS 2011).

Corresponding procedures are provided by § 5 subsection 2 Groundwater Ordinance which controls the procedure in case the threshold is exceeded due to geogenic background concentrations: "... the competent authority defines a different threshold considering the background value for this groundwater body. The background value is the ninetieth percentile of the distribution of the substance concentrations in the groundwater of the hydrogeological unit decisive for the groundwater body."

For the current derivation of the GFS value, the basic value was used accordingly instead of the ecotoxicological thresholds as GFS value if the environmental quality standard or the PNEC value is less than or equal to the basic value.

² In other publications, the terms "safety factor" or "transmission factor" may be used synonymously with the term "compensation factor".

GFS derivation 2004		GFS derivation 2016
1. Environmental quality standard	===	1. EQS of OGewV (without human fish consumption and "secondary poisoning")
2. PNEC _{aquat.}	===	2. EU-agreed PNEC _{aquat.} (RAR final. o. draft); EQS IKSR)
3. LAWA ZV	¥	LAWA ZV are no longer relevant and have been replaced by EQS (OGewV)
4. MPA	¥	Like the other Member States, the Netherlands define EQS; MPA that are still valid are listed under Others
5. Others: Substance evaluations that are discussed and accepted in the professional public, especially on EU level; usually no consideration of individual test results	===	3. Others: Proposals for EQS if compliant with Lepper 2005 and in the future TGD-EQS 2011 by Member States of the EU or accepted institutions (e.g. IKSR, RIVM) submitted for the protection of the aquatic biocoenoses; as exception, non-agreed PNEC (e.g. derivation by state authorities)
2), 3), 4) + 5) the basic value is added to the value	¥	Addition of the basic value is omitted. For 1), 2) + 3), the GFS value is limited to the basic value.

Table 1: Comparison of the GFS derivation 2004 and 2016

2.2.3 Checking the derived values for plausibility

The results from urgent and longer-term mono species tests at algae, invertebrates and fish usually form the basis for the derivation of the PNEC. The PNEC results from the lowest test result divided by a compensation factor which - depending on the data available -

varies between 10 and 1,000. So consequently, PNEC values may change if an improved data basis is available. That is why one introduced the possibility to not take over a $PNEC_{aquat}$. If the consideration of current data leads to a considerable change in the derived value or for an essential substance, the derived value is clearly below the background/basic value.

Even if ecotoxicologically justified GFS are often below human toxicologically justified values, it must - for cases for which only ecotoxicological evaluations are available - be shown in a plausible form that such justified GFS also reasonably consider human health, which is generally regarded as important subject of protection. Such plausibility check is to be completed based on the concept of the health orientation value (HOV) of the Federal Environment Agency (UBA, 2003: Dieter, 2003). Depending on the toxicological database and known effect of a substance to be evaluated, GOW are graded between 0.01 and 10 µg/l. This range covers the entire quantity of the completely evaluable substances soluble in water that have been assessed until now. The GOW are graded so that a substance is even evaluated correctly if upon completion of its data basis it turns out that the most unfavourable possibility is applicable. If, for example, genotoxic effects are known for a substance, the GOW may be lower or - if negative, neurotoxic studies for a verifiably non-genotoxic substance are known - it may be higher (UBA, 2003, Dieter, 2003). According to this concept, it is very probable that the GOW is within the precautions range. It is therefore determined that the result of the ecotoxicological evaluation is still accepted as GFS if it is above the corresponding GOW up to a factor of three. This difference is still within a range that is to be regarded as toxicologically equal. If the human toxicological criteria are not sufficient to derive a GFS value, the GOW with its precautionary character will prevent the definition of a value that might be too high and exclusively be based on the ecotoxicological evaluation.

For substances which have not been finally evaluated until now or the derived GFS of which are within a very low concentration range, a minimum limit value will be fixed. As orientation for

this limitation, one once again uses the GOW that - also according to a recommendation by the Drinking Water Committee of the Federal Ministry of Health and Social Security (BMG) - limits the presence of substances in drinking water, which are not or only incompletely evaluable from a human toxicological point of view to a level of 0.1 μ g/l . "Strongly genotoxic substances" are excluded for which a value of 0.01 μ g/l applies in case of lifelong exposure (UBA, 2003; Dieter, 2003). As ecotoxicological effects often occur at lower loads than human toxicological effects, the lower GFS limit is selected lower than the recommended GOW of 0.1 μ g/l. In order to allow for both, the frequently decisive ecotoxicological relevance of substances and the analytical determinability, the lower GFS limit is set to 0.01 μ g/l.

The following exceptions apply:

- Substances for which effects at concentrations of less than 0.01 µg/l can be proven and
- Substances with legally binding environmental quality standards and substances with PNEC_{aquat} of less than 0.01 μg/l, which are agreed all over Europe.

2.3 Methodology for substance aggregates

The insignificant threshold values are derived on the basis of effective data for individual substances. In practice, chemically similar compounds are often summarized in substance groups (e.g. polycyclic aromatic hydrocarbons – PAH, polychlorinated biphenyles – PCB, alkylated monoaromatics – BTEX including benzene and highly volatile halogenated hydrocarbons – VHH) and also occur together in the environment. The composition of the mixtures to be evaluated varies; thus, it is hard to predict the effective strength of mixtures. As the effect of mixtures cannot or only insufficiently be evaluated, a maximum limit for the total of individual substances must be fixed.

The values specified in Annex 2 accordingly consider both, insignificant threshold values for individual substances - if available - and substance aggregates. The justification for the use of the substance aggregates is contained in the substance data sheets in Annex 3.

3 Principles for the use of the insignificant threshold values

The GFS values serve the protection of the groundwater in the precaution and follow-up care area. Applications include pollutant entries at points and/or groundwater loads from point sources.

Figure 1 shows possible applications of the GFS values.



Fig. 1: Applications of the insignificant threshold values

The applications in water legislation include in particular the use of water bodies such as direct discharge and the entry of solid substances into the groundwater.

Apart from that, the GFS values may serve as basis for evaluations in connection with the implementation of the Water Framework Directive (see chap. 3.1.3). In this connection, it has to be noted that the reference levels differ (local, referring to the groundwater, or condition evaluation referring to the groundwater bodies).

The GFS values may also be used as basis for evaluations of groundwater pollution for which it can be proven that they have not been introduced via the soil.

The GFS values are also relevant for the utilisation of waste as well as the application and entry of materials onto or into the soil. The substance release from buildings above the groundwater must also be considered. Here, it is about the evaluation of the consequences on the groundwater, e.g. considering the material and product specifications, the type of installation into the soil and/or into technical buildings and the (natural) soil quality (including quality of the soil leachate) (see chap. 3.2).

In the follow-up soil protection, the GFS values form the basis for updating the test values for the effective path soil-groundwater and the specifications for their application in BBodSchV.

The following chapters 3.1 to 3.3 contain explanatory notes on the principles of the application of the GFS values in the relevant legal areas of the Water, Waste and Soil Protection Act.

3.1 Application in the water legislation

3.1.1 Precautionary water protection

In general, every use of a water body requires an approval. Any actual use which may lead to changes in substance concentrations in the groundwater include in particular

- the entry and introduction of substances into the groundwater (§ 9 subsection 1 no. 4 WHG) [German Federal Water Act - WHG] as well as
- measures that are capable of bringing about permanent or not only irrelevant detrimental changes in the groundwater quality (§ 9 subsection 2 no. 2 WHG).

Any granting of an approval for the groundwater use is excluded (§ 12 subsection 1 WHG) if **detrimental** changes in the water body have to be expected that cannot be avoided or compensated by incidental provisions either or if other requirements from public law are not fulfilled. The term **detrimental changes in water bodies** (§ 3 no. 10 WHG) refers to changes in the properties of water bodies (e.g. water quality, water quantity, see § 3 no. 7, 9 WHG) impairing the well-being of the general public, particularly the public water supply or not complying with the requirements resulting from

- the Federal Water Act,
- regulations enacted on the basis of the Federal Water Act or
- other legal water regulations.

To keep the groundwater clean the requirements of § 48 WHG (axiom of concern) have to be observed: A permit for the entry and introduction of substances into the groundwater may only be granted if any detrimental change in the water quality does not have to be concerned (§ 48 subsection 1 WHG). Substances may only be stored or deposited in a form that any detrimental change in the groundwater quality does not have to be concerned (§ 48 subsection 2 WHG). A **concern** is already at hand if there is only the lowest probability that a detrimental change will occur according to human experience.

The change in the water quality is **detrimental** if it constitutes an **impairment that is not only negligible**, as compared to the natural groundwater quality. The GFS values will be used when verifying the question whether with the projected or determined substance concentrations, **a detrimental change** in the (ground) water quality has to be concerned due to an intended action or concretely applied groundwater use. For the approval of groundwater use, other standards may moreover be relevant referring to the permanence of the substance entries and/or the substance loads.

It is the task of the competent water authority to evaluate these points in the individual case. The standard of the GFS concept provides related support. This results in simplified enforcement and foreseeable decisions for the user of the water body. This provides for planning safety whether intended actions will probably comply with the water law requirements and are approvable or cannot be approved.

3.1.1.1 Entry or introduction of substances into the groundwater (use according to § 9 subsection 1 no. 4 WHG)

If the GFS values are complied within the medium to be introduced, possibly with lower total loads, § 48 subsection 1 WHG rules that a detrimental change in the water quality does not have to be feared and thus, there is no ground for refusal in the sense of § 12 subsection 1 WHG - referring to a possible pollutant entry to be evaluated according to the standard of the GFS values.

If the GFS values are reached or exceeded or if not only irrelevant substance loads are introduced into the groundwater, this does not mean that an approval cannot be granted. In case of a possible exceedance of the GFS values, the possibility to grant an approval regarding groundwater use shall rather be checked further considering the local or regional conditions, the duration and the spatial expansion of the exceedance as well as the transferable **substance loads**.

If - when checking the individual case using the GFS values and the loads - the water authority comes to the result that a detrimental change in the relevant groundwater quality according to § 48 subsection 1 WHG has to be feared so that the granting of an approval for the entry or introduction into the groundwater is ruled out (§ 48 subsection 1 WHG), there is - according to the water law systematics and in normative terms - a detrimental change in the groundwater that has to be expected according to § 12 subsection 1 no. 1 in connection with § 3 no. 10 WHG.

The "LAWA-Hinweise für die Anwendung der Geringfügigkeitsschwellenwerte bei Benutzungen des Grundwassers in bestimmten Fallgestal tungen" (LAWA, 2006) that were published in 2006 contain detailed information dealing with the introduction of substances into the groundwater. Compliance with the GFS values in the contact area between construction product and groundwater is also part of the DIBt principles for the evaluation of the effects of construction products on soil and groundwater (DIBt, 2011) according to which substance entries by construction products into the groundwater are evaluated. With a corresponding evaluation of construction products that are used in the groundwater, the GFS values are also regarded as having been complied with if the average substance concentrations do not exceed the GFS values only for a short period and for a spatially limited volume. The undefined terms "short period" and "spatially limited volume" are to be specified in the individual case in the water law procedure and as general rules by LAWA.

3.1.1.2 Entry of substances into the groundwater (pseudo use according to § 9 subsection 2 no. 2 WHG)

Activities and circumstances that may lead to the entry of substances into the groundwater in an indirect way are also to be evaluated as actual use according to § 48 subsection 2 WHG according to the axiom of concern or in certain cases according to § 9 subsection 2 no 2 WHG. If the substance enters through the water-unsaturated soil zone, the place of evaluation and/or prognosis whether the GFS values are not reached is the leachate upon entry into the groundwater. It may additionally be necessary to consider the substance loads entering the groundwater so that permanent or considerable detrimental changes in the groundwater quality don't have to be concerned.

If the prognosis shows that the GFS values will be exceeded upon entry into the groundwater or that not only low substance loads will be available, this is to be considered an actual use according to § 9 subsection 2 no. 2 WHG in each case. The possibility to grant an approval is to be checked in more detail in the individual case.

More detailed information is also contained in the "*Grundsätze des vorsorgenden Grundwasserschutzes bei Abfallverwertung und Produkteinsatz*" (so-called GAP paper, LAWA, 2002) published in 2002 which deal with the requirements on the indirect introduction of substances into the groundwater. For such cases, compliance with the GFS values is also part of the DIBt principles for the evaluation of the effects of construction products on soil and groundwater (DIBt, 2011).

For the evaluation of extensive (diffuse) entries - e.g. atmospheric depositions or the consequences of agricultural fertilising measures - the GFS values have not be derived and are thus not provided.

3.1.2 Follow-up water protection

As the exceedance of the GFS values is only one assessment factor when evaluating the detriment of a change in the groundwater quality, the fact that the GFS values in the groundwater have been reached or exceeded by an already occurred immission do not yet cause prejudice with regard to the evaluation whether **remediation measures** are necessary or not. In this connection, the enforcement authorities have a scope of discretion in the overall evaluation of the situation. Regarding the occurrence of a detrimental change in the water body, we also refer to chap. 3.3. The principle of proportionality is to be observed. More detailed information is currently contained in the "*Grundsätze des nachsorgenden Grundwasserschutzes bei punktuellen Schadstoffquellen*" (LAWA-LABO, 2006) jointly published in 2006 by LAWA and LABO and in tools worked out by the federal states (e.g. Classification and rehabilitation of groundwater contaminations GWS-VwV, 2005). Reference is made to the consideration of the geogenic background value for those substances which are naturally available in the groundwater (Wagner et al., 2014; see also chap. 2.2.2).

3.1.3 Assessment of the status of ground water according to the Groundwater Ordinance (GrwV, 2010)

The Ordinance for the Protection of the Groundwater (Groundwater Ordinance - GrwV) defines "thresholds" as concentration of a pollutant or a group of pollutants that are defined for the protection of human health and the environment (§ 1 no. 1 GrwV). The threshold values form the **basis for the evaluation** of the chemical groundwater quality and serve the implementation of the EC Water Framework Directive and the EU Groundwater Directive from the year 2006 into national law. Reference is particularly made to §§ 5, 13 GrwV.

The German threshold values in the GrwV have been developed due to the derivation systematics for the GFS values, are, however, currently provided with a low parameter spectrum. The GFS values can be used for the determination of other threshold values by the competent authority if there is a risk for a groundwater body with regard to the chemical quality by a substance or group of substances not listed in Annex 2 to the GrwV.

Inorganic trace elements may naturally occur in increased concentrations. If the regional or local geogenic background values in the groundwater exceed the GFS values, the competent authorities may define differing threshold values according to the specifications of the Groundwater Ordinance.

3.2 Application of soil protection and waste legislation – Precaution

The precaution against detrimental changes in the groundwater quality is based on § 48 WHG (see also chap. 3.1). § 7 BBodSchG and § 7 subsection 3 KrWG refer to precautionary legal water provisions that also apply to substance releases from mineral materials. Insofar, it has to be ensured that the insignificant threshold values are complied when these substances enter the groundwater. To do so and from the point of view of precautionary groundwater protection, the value level of the GFS is transferred to the place of evaluation, i.e. the entry of the leachate from the unsaturated zone into the groundwater. Precautionary soil protection and legal water regulations coexist. The precautionary obligation under soil protection law limits the substance release into the soil irrespective of the effective path in case of exceedance of the precautionary values and aims to prevent the occurrence of detrimental soil changes (§§ 7 and 8 BBodSchG).

Soil material complying with the precautionary values according to BBodSchV and for which there is no suspicion of other specific contaminations satisfies both, the requirements of precautionary soil protection and the requirements of precautionary groundwater protection. Substance releases as a consequence of the utilization of mineral replacement construction materials in technical structures as well as the

Introduction of material below/outside the soil layer penetrable by roots are to be limited so that the GFS values at the place of evaluation are safely and continuously complied with. If replacement construction materials are used in defined installation methods, the GFS values for substances that cannot be retarded are also regarded as having been complied with if the average substance concentrations only for a short period and for a spatially limited volume exceed the GFS values. When estimating the substance concentrations in the leachate upon entry into the groundwater, the decomposition and retention ability of the unsaturated soil zone can be considered to a limited extent. The aspect of variability and uncertainty regarding the determining soil characteristics and the substance concentrations should be considered.

Depending on sorption-determining soil characteristics such as the physical-chemical environment, inorganic substances are - in the unsaturated soil zone - also transferred from natural, unloaded soil into the dissolved phase. According to today's knowledge, this does not have a detrimental effect on the chemical groundwater quality. For the evaluation of substance releases in the unsaturated soil zone, the GFS values are regarded as having been complied with at the place of evaluation if the concentrations of the pollutants in the leachate do not exceed the natural background value level for substances in the leachate. The concentration of the substances in the leachate is estimated by the examination of eluates. In this connection, the evaluation of substance releases in watery eluates must refer to the same water/solid ratio as was also used for the derivation of the background values.

3.3 Hazard assessment and control in the application of soil protection legislation – Follow-up care

In the treatment of detrimental soil changes, legacies, suspicious areas and areas with suspected legacy for the effective path soil-ground water, overlaps result between water and soil protection legislation.

The test values according to soil protection legislation that are to be defined according to § 8 subsection 1 sentence 2 no. 1 BBodSchG serve the risk assessment. There is usually a reasonably suspected risk if test values have been exceeded. In this case, the competent authority may - according to § 9 subsection 2 BBodSchG - order the obligor to carry out a detailed examination. The test values may also serve as basis for the final assessment whether there are risks, considerable disadvantages or considerable inconvenience for the individual or the general public with regard to the relevant effective path (detrimental changes in the soil and/or legacy) if other scales are not available. Test values for the effective path soil-groundwater refer to the transitional area from the unsaturated into the saturated soil zone (place of the evaluation).

The insignificant threshold values derived by means of this report are the decisive technical basis for the future definition of the BBodSchV test values for the effective path soil-groundwater.

The following application principles are to be considered in the definition and application of test values (suspicion evaluation) and/or in the question whether there is a detrimental change in the groundwater or such change is to be expected (risk assessment):

- 1. The substance is entered into the groundwater via the leachate. With a water/solid ratio (W/F) of 2 l·kg⁻¹, eluates from uncontaminated soils in Germany show concentrations clearly above the GFS for numerous inorganic substances (Utermann, 2011). If the leachate is characterised by an eluate gained according to this method, only clear exceedance of the concentration level that is naturally to be expected in the unsaturated soil zone will indicate a suspected risk for these substances.
- 2. When estimating the substance entry into the transitional area from the unsaturated into the saturated soil zone, the decomposition and retention ability of the unsaturated zone is to be considered (leachate prognosis).

- 3. The place of the evaluation of the leachate is risk source for the groundwater according to BBodSchV is generally the transitional area from the unsaturated into the saturated zone. The GFS values for the groundwater refer to a groundwater volume accessible for measurements. If the admissible leachate concentration at the place of evaluation is exceeded, the mixing process of the leachate with the groundwater can be brought to account in a limited volume if the hydrogeological boundary conditions are suitable (admixing prognosis).
- 4. For the evaluation of existing substance concentrations in the groundwater or those to be expected in the near future within the scope of the examination of suspicious areas or areas with suspected legacy, the GFS values are generally suitable. For inorganic substances, the ecotoxicological effective thresholds of which are below geogenic background concentrations in the groundwater, the basis values have been referred to as GFS values. In order to get a suitable distance to background concentrations, a suspected risk is only assumed in the evaluation of substance concentrations at the place of the assessment if twice the basic value is exceeded. This procedure does not apply to human toxicologically justified evaluations.
- 5. In order to allow for targeted consideration of the relevant objects of protection in the risk assessment, it can be checked in the individual case considering the derivation methodology of the GFS values which of the two protection objectives according to Annex 1 (I or II) was decisive for the derivation. If the substance concentrations in the groundwater exceed the thresholds of the heath/sensory effect (I), there is in any case a detrimental change in the water body. If the substance concentrations fall below the thresholds of the health/sensor effect (I) exceed, however, the thresholds for the ecotoxic effect (II), it has to be checked to what extent surface water bodies or groundwater-dependent terrestrial ecosystems may be impaired.

The fact that exceedance of the GFS values in the groundwater results in a detrimental change in the groundwater quality applies irrespective of the application principles. Whether the extent of such change is sufficient to justify the suspicion of or an actual detrimental soil change with regard to the effective path soil-groundwater or a detrimental change in the water body within the frame of the water law follow-up care (3.1.2) can be determined considering the above-mentioned principles.

The application principles do, however, not finally describe a suspected risk, an actual risk and/or a detrimental change in a water body either. Risk-triggering thresholds may consider other criteria and boundary conditions specific for the individual case. It must for example be considered if there are locally or regionally higher geogenic background concentrations in the individual case than those of twice the basic value in a groundwater region and/or a hydrogeochemical unit.

According to § 4 subsection 4 BBodSchG, the requirements to be satisfied **in the remediation** of water bodies are determined according to the water law. The insignificant threshold values that first of all only indicate a detrimental change in the groundwater quality are not to be directly used as rehabilitation targets for the groundwater. Rehabilitation targets are to be defined on a case-by-case basis. Rehabilitation targets do not only emphasize concentrations, but also have to consider other evaluation criteria (e.g. freight in the groundwater) and follow the principle of proportionality. In this connection, the preceding considerations may also be used.

4 Analytics

More detailed information regarding the analytics of the individual substances and/or parameters of Annex 2 is provided at the end of the relevant data sheet.

Almost exclusively, "Deutsche Einheitsverfahren (DEV)" that have mainly been transformed into DIN standards and sometimes into European (EN) or international standards (ISO), are specified. The specified analysis procedures are in each case to be used in their current

version. Use of equal procedures is admissible if they are suitable for monitoring compliance with the GFS. The lower application limits are both, substance- and matrix-dependent. For some of the specified procedures, the lower application limit is higher than or equal to the insignificant threshold value. Here it is necessary- in the individual case - to make use of non-standardised procedures that are to be validated and to be described according to the relevant rules for analysis procedures.

5 Explanation of the annexes

<u>Annex 1</u> contains an overview scheme of the methodology presented in chapter 2 for the derivation of the insignificant threshold values.

The insignificant threshold values derived according to this methodology for individual substances and for aggregate parameters are documented in a tabular overview in <u>Annex 2</u>.

<u>Annex 3</u> contains the data sheets for the individual substances and groups of substances for which insignificant threshold values have been derived. All data sheets are preceded by a tabular short version with information on the insignificant threshold values, on the available data material and on the criteria which provide the decisive justification regarding the derivation of the insignificant threshold value. If this clearly shows which criteria have led to the derivation of the GFS value, a detailed justification is usually omitted. A detailed justification is necessary if reference to corresponding sources (e.g. TrinkwV) is not possible. In this case, the data sheet will - in addition to a detailed justification of the insignificant threshold value - also contain the literature sources used. Basic values are only specified for inorganic trace substances.

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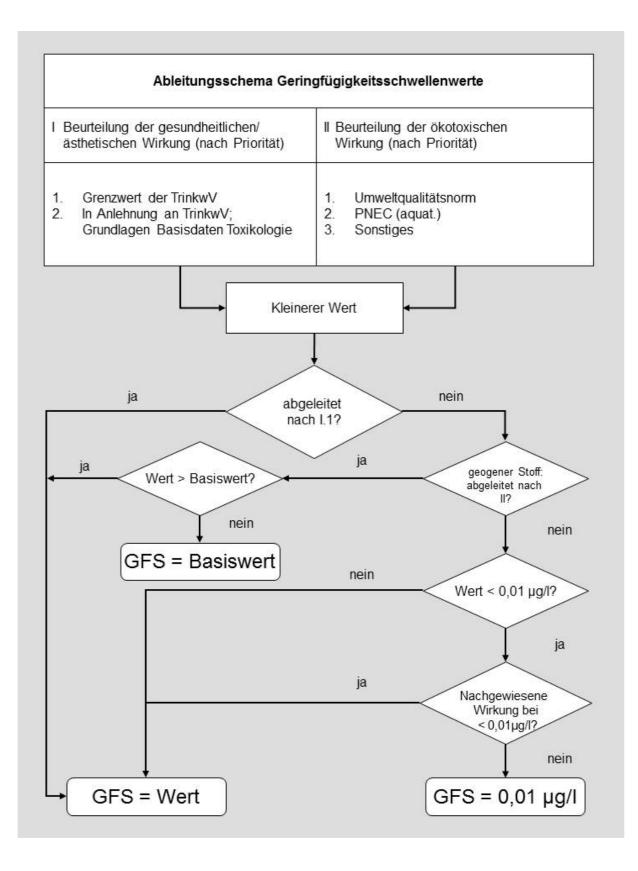
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Annex 1:

Derivation scheme of the insignificant threshold values



Annex 2:

Insignificant threshold values (GFS values) for the evaluation of locally restricted ground water changes

Part 1 – Inorganic parameters

Parameter	CAS no.	GFS value µg/l	Analysis procedure
Antimony	7440-36-0	5	DIN 38405-32:2000-05; DIN EN ISO 17294-2:2005-02
Arsenic	7440-38-2	3.2	ISO 17378-2:2014-02; DIN EN ISO 17294- 2:2005-02
Barium	7440-39-3	175	DIN EN ISO 11885:2009-09; DIN EN ISO 17294-2:2005-02
Lead	7439-92-1	1.2	DIN 38406-6-2:1998-07; DIN EN ISO 17294-2:2005-02
Boron	7440-42-8	180	DIN 38405-17:1981-03; DIN EN ISO 11885:2009-09; DIN EN ISO 17294-2:2005- 02
Cadmium	7440-43-9	0.3	DIN EN ISO 5961-HA3:1995-05; DIN EN ISO 17294-2:2005-02
Chromium	7440-47-3	3.4	DIN EN 1233:1996-08; DIN EN ISO 17294- 2:2005-02
Cobalt	7440-48-4	2.0	DIN 38406-24-2:1993-03; DIN EN ISO 15586:2004-02; DIN EN ISO 17294-2:2005- 02
Copper	7440-50-8	5.4	DIN 38406-7-2:1991-09; DIN EN ISO 17294-2:2005-02
Molybdenum	7439-98-7	35	analogously DIN EN ISO 5961:1995-05; DIN EN ISO 11885:2009-09; DIN EN ISO 17294- 2:2005-02
Nickel	7440-02-0	7	DIN 38406-11-2:1991-09; DIN EN ISO 11885:2009-09; DIN EN ISO 17294-2:2005- 02
Mercury	7439-97-6	0.1	DIN EN ISO 12846:2012-08; DIN EN ISO 17852:2008-04
Selenium	7782-49-2	3	DIN 38405-23-2:1994-10 DIN EN 17294-2:2005-02
Thallium	7440-28-0	0.2	DIN EN ISO 17294-2:2005-02
Vanadium	7440-62-2	4	
Zinc	7440-66-6	60	DIN EN ISO 11885:2009-09; DIN EN ISO 17294-2:2005-02
Chloride	16887-00-6	250 mg/l	DIN EN ISO 10304-1:2009-07; DIN EN ISO 10304-4:1999-07
Cyanide easily released / complex	57-12-5	10 / 50	DIN 38405-7:2002-04; DIN 38405-13:2011- 04; DIN EN ISO 14403:2012-10
Fluoride	16984-48-8	900	DIN 38405-4:1985-07; DIN EN ISO 10304- 1:2009-07
Sulphate	14808-79-8	250 mg/l	DIN EN ISO 10304-1:2009-07

Annex 2:

Insignificant threshold values (GFS values) for the evaluation of locally restricted ground water changes

Part 2 – Organic parameters

Parameter	CAS no.	GFS value µg/l	Analysis procedure	
Industrial chemicals and	other parame	ters		
PAH ¹⁾ , total		0.2		
Anthracene	120-12-7	0.1		
Benzo[a]pyrene	50-32-8	0.01		
Total benzo[b]fluoranthen e and benzo[k]fluoranthen e	205-99-2 207-08-9	0.03	DIN EN ISO 17993:2004-03 ⁴⁾ ; DIN 38407-39:2011-09 ⁵⁾ DIN ISO 28540:2014-05 ⁴⁾	
Total benzo[ghi]perylene and indeno[123- cd]pyrene	191-24-2 193-39-5	0.002		
Dibenz[a, h]anthracene	53-70-3	0.01		
Fluoranthene	206-44-0	0.1		
Naphthalene and methyl-naphthalene, total	91-20-3 90-12-0 91-57-6	2		
VHH ²⁾ , total		20		
Tri- and tetrachloroethylene, total	79-01-6 127-18-4	10	DIN EN ISO 10301:1997-08; DIN EN ISO 15680:2004-04	
1,2-dibromoethane	106-93-4	0.02	DIN 38407-43:2014-10	
1,2-dichloroethane	107-06-2	3		
Trichloromethane	67-66-3	2.5		
Chloroethene (vinyl chloride)	75-01-4	0.5	DIN EN ISO 15680:2004-04 DIN 38407-43:2014-10	
Polychlorinated biphenyles (PCB) ³⁾ , total	1336-36-3	0.01 (0.0005 in each case for PCB-28, -52, - 101, -118, -138, - 153 and -180)	DIN 38407-2:1993-02 ⁴⁾ ; DIN EN ISO 6468:1997-02 ⁴⁾ ; DIN 38407-3-1:1998-07 ⁴⁾ DIN 38407-37:2013-11 ⁴⁾	
Hydrocarbons		100	DIN EN ISO 9377-2:2001-07	
Benzene and alkylated benzenes, total		20	ISO 11423:1997-06; DIN 38407-9:1991-05; DIN EN ISO 15680:2004-04; DIN 38407-43:2014-10	
Benzene	71-43-2	1	DIN EN ISO 15680:2004-04 DIN 38407-43:2014-10	
Ether oxygenate (especially MTBE, ETBE and TAME), total	1634-04-4 (MTBE) 637-92-3 (ETBE) 994-05-8 (TAME)	5, thereof max. 2.5 μg/l ETBE	DIN 38407-41:2011-06 DIN 38407-43:2014-10	
Epichlorhydrin	106-89-8	0.1	DIN EN 14207:2003-09 ⁴⁾	
Phenol	108-95-2	8	ISO 8165-2:1999-07; DIN 38407-27:2012-10	

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Nonylphenol	25154-52-3 (Isomer mixture) 84852 15-3 (4-nonylphenol, branched)	0.3	DIN EN ISO 18857-1:2007-02 DIN EN ISO 18857-2:2012-01
Chlorophenols, total		1	DIN EN 12673:1999-05
Pentachlorophenol	87-86-5	0.1	DIN EN 12673.1999-05
Chlorobenzene, total		1	DIN EN ISO 10301:1997-08; DIN 38407-43:2014-10 (only for Cl ₁ -Cl ₃) DIN EN ISO 6468:1997-02; DIN 38407-2:1993-02; DIN 38407-37:2013-11 (only for Cl ₃ – Cl ₆)
Trichlorobenzene		0.4	DIN EN ISO 10301:1997-08; DIN EN ISO 6468:1997- 02; DIN 38407-37:2013-11; DIN 38407- 43:2014-10
Pentachlorobenzene	608-93-5	0.007	DIN EN ISO 6468:1997-02; DIN 38407-2:1993-02;
Hexachlorobenzene	118-74-1	0.01	DIN 38407-37:2013-11

PSMBP, total		0.5	Low-volatile HHC and organochlorine
PSMBP, individual substance		in each case 0.1	 pesticides⁶:DIN 38407- 2:1993-02; DIN EN ISO 6468:1997-02; DIN 38407- 37:2013-11 Organ. N and P compounds⁷⁾:DIN EN ISO 10695:2000-11, DIN EN ISO 11369:1997-11; DIN EN 12918:1999-11 Phenoxyalkanecarboxylic acid herbicides:DIN 38407- 14:1994-10, DIN ISO 15913:2003-05; DIN 38407- 35:2010-10 Selected PSMBP by means of HPLC-MS/MS after direct injection: DIN 38407-36:2014-09
Azinphos-methyl	86-50-0	0.01	DIN EN 12918:1999-11 ⁴⁾
Chlordane	57-74-9	0.003	DIN 38407-37:2013-11
Cyclodien pesticides, total (aldrin, dieldrin, endrin and isodrin)	309-00-2 60-57-1 72-20-8 465-73-6	0.01	DIN 38407-2:1993-02 DIN EN ISO 6468:1997-02 DIN 38407-37:2013-11
Dichlorvos	62-73-7	0.0006	DIN EN 12918:1999-11 ⁴⁾
Disulfoton	298-04-4	0.004	No standardized procedure available ⁵⁾ Recommendation: DIN EN 12918:1999-11
Diuron	330-54-1	0.1	DIN EN ISO 11369:1997-11 DIN 38407-36:2014-09
Endosulfan	115-29-7	0.005	DIN 38407-2:1993-02; DIN EN ISO 6468:1997-02; DIN 38407-37:2013-11
Etrimfos	38260-54-7	0.004	No standardized procedure available ⁵⁾ Recommendation: DIN EN 12918:1999-11
Fenitrothion	122-14-5	0.009	DIN EN 12918:1999-11 ⁴⁾
Fenthion	55-38-9	0.004	Din Lin 12910.1999-11
Heptachlor	76-44-8	0.03	DIN 38407-2:1993-02; DIN EN ISO 6468:1997-02;
Heptachlor epoxide	1024-57-3	0.03	DIN 38407-37:2013-11
Hexazinone	51235-04-2	0.07	DIN EN ISO 11369:1997-11 DIN 38407-36:2014-09
Malathion	121-75-5	0.02	DIN EN 12918:1999-11 ⁴⁾
Mevinphos	7786-34-7	0.0002	No standardized procedure available ⁵⁾ Recommendation: DIN EN 12918:1999-11
Parathion-ethyl	56-38-2	0.005	DIN EN ISO 10695:2000-11; DIN EN 12918:
Parathion-methyl	298-00-0	0.02	1999-11 ⁴⁾
Pentachlorophenol	87-86-5	0.1	DIN EN 12673:1999-05 ⁴⁾

Parameter	CAS no.	GFS value μg/l	Analysis procedure
Phoxim	14816-18-3	0.008	DIN 38407-36:2014-09 ⁴⁾
Triazophos	24017-47-8	0.03	No standardized procedure available ⁵⁾ Recommendation: DIN EN 12918:1999-11
Trichlorfon	52-68-6	0.002	No standardized procedure available ⁵⁾
Trifluralin	1582-09-8	0.03	DIN EN ISO 10695:2000-11

Tin-organic compounds			
DibutyIltin cation	14488-53-0	0.01	
TributyIltin cation	36643-28-4	0.0002	DIN EN ISO 17353:2005-114)
Triphenyltin cation	668-34-8	0.0005	

Compounds typically contained in explosives			
Nitropenta (PETN)	78-11-5	10	DIN EN ISO 22478:2006-07
2-nitrotoluene	88-72-2	1	
3-nitrotoluene	99-08-1	10	
4-nitrotoluene	99-99-0	3	
2-amino-4,6-dinitrotoluene	35572-78-2	0.2	DIN 38407-17:1999-02 ⁴⁾
4-amino-2,6-dinitrotoluene	19406-51-0	0.2	DIN EN ISO 22478:2006-07 ⁴⁾
1,3-dinitrobenzene	99-65-0	0.3	
2.4-dinitrotoluene	121-14-2	0.05	
2.6-dinitrotoluene	606-20-2	0.05	
1,3,5-trinitrobenzene	99-35-4	8	
2,4,6-trinitrophenol (picric acid)	88-89-1	0.2	DIN EN ISO 22478:2006-07
2,4,6-trinitrotoluene	118-96-7	0.2	DIN 38407-17:1999-02; DIN EN ISO 22478:2006-07
Hexogen	121-82-4	1	
Hexanitrodiphenylamin e (hexyl)	131-73-7	2	DIN EN ISO 22478:2006-07
Nitrobenzene	98-95-3	0.1	DIN 38407-17:1999-02
Tetryl	479-45-8	5	DIN EN ISO 22478:2006-07
Octogen	2691-41-0	175	Din Lin ISU 224/ 0.2000-07

1) PAH total: Total of the polycyclic aromatic hydrocarbons without naphthalene and methylnaphthalene, usually determination by means of the total of 15 individual substances according to the list of the US Environmental Protection Agency (EPA) without naphthalene; considering other relevant PAH (e.g. aromatic heterocyclic substances such as chinoline), if applicable

 VHH, total: Highly volatile halogenated hydrocarbons, i.e. Total of the halogenated C1 and C2 hydrocarbons; including trihalogenmethane. The GFS values for tri and tetrachloroethene, dichloroethane and chloroethene must moreover be complied with. (10 Σ tri and tetrachloroethene, 10 Σ other VHH)

3) PCB, total: Total of the polychlorinated biphenyles; total of the 6 PCB congeners (PCB-28, -52, -101, -138, -153, and -180) multiplied by factor 5.

4) If no standardized procedure is available by means of which the insignificant threshold values can be reached or undershot, nonstandardized procedures have to be made use of which are to be validated according to the relevant rules for analysis procedures. The procedure is to be described.

5) For many PSMBP compounds, no standardised procedures are available. Alternatively, standardised procedures for the determination of structurally similar compounds can be used like e.g. In the group of organochlorine pesticides or the organic N and P compounds or standardised procedures using HPLC-MS/MS technology allowing for a very sensitive and specific determination of numerous compounds. The analysis procedures have to be validated for the compounds to be determined according to the relevant rules.

6) E.g. cyclodien pesticides (aldrin, dieldrin, endrin, isodrin), DDT, HCH isomers, endosulfan, heptachlor.

7) Selected organic N and P compounds, e.g. triazine herbicides, phenylurea herbicides, organophosphoric acid derivatives