Länderarbeitsgemeinschaft Wasser (LAWA)

Determination of insignificance thresholds for groundwater

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The insignificance thresholds data sheets (Annex 3) are available as a booklet from Kulturbuchverlag (in German only; they are not available online).

1 Introduction

Standardised national criteria for the assessment of existing groundwater contamination or the risk thereof are needed if such assessments are to be viable and applicable across the board. The greatest need in this regard is for a quality standard that defines the substance concentration threshold for (a) a low level of locally defined anthropogenic change in the chemical properties of groundwater; and (b) the substance concentration for groundwater pollution. The Working Group of the Federal States on Water Issues (Länderarbeitsgemeinschaft Wasser (LAWA)) has determined that the insignificance threshold is a suitable quality standard for this purpose. The insignificance threshold delineates the borderline between insignificant change in the chemical properties of groundwater and harmful contamination.

In late 1998 an ad-hoc LAWA working group issued, but failed to adopt, a report entitled *Geringfügigkeitsschwellen (Prüfwerte) zur Beurteilung von Grundwasserschäden und ihre Begründung* (Insignificance thresholds (guidance values) for the assessment of groundwater pollution and the attendant computation methodologies).

The Soil Protection Act (Gesetz zum Schutz des Bodens (BBodSchG)) and the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV)), which were enacted in 1998 and 1999 respectively, modified the statutory regulations governing the extent to which percolation water falls within the purview of the Federal Soil Protection Ordinance and groundwater falls within the purview of federal water legislation.

In October 1999, the 24th Senior Officials Conference (24. Amtschefkonferenz (ACK)) instructed the Joint Federal State Soil Protection Commission (Bund/Länder-Arbeitsgemeinschaft Bodenschutz (LABO)) as well as the Working Group of the German Laender on Water, Waste and Immission Protection (Länder- Arbeitsgemeinschaften Wasser, Abfall und Immissionsschutz (LAWA, LAGA and LAI)) to review, under the auspices of LABO, all soil contamination values that are regulated under German law.

At its 114th general meeting on February 2000, LAWA took the initial step of defining as insignificance thresholds the soil contamination values mandated by the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV)), and in so doing decided to elaborate recommendations aimed at extending the life of existing regulatory values relating to the soil-groundwater exposure pathway.

In its October 2000 report entitled *Harmonisierung der den Boden betreffenden Werteregelungen* (Harmonization of soil related regulatory values), LAWA put forward the following harmonization recommendation (inter alia) at the behest of the Senior Officials Conference Working Group on the Soil-Ground Exposure Pathway:

"Some of the parameters for the soil-groundwater exposure pathway guidance values laid down in Annex 2(3.1) of the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV)) are inconsonant with those elaborated by LAWA's ad-hoc Guidance Values working group (as at 21 Dec. 1998, LAWA 1998). LAWA should be asked to compile lists of the following elements that are to be included in a proposed extension of the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV)): insignificance thresholds relating to the assessment of groundwater contamination, the attendant determination standards, and any other substances that are relevant for contaminated sites."

The rationale for this recommendation was as follows (in part):

"In view of the fact that definition standards for the guide values that apply to assessment of the soil-groundwater exposure pathway are mandated by federal water legislation, it is safe to assume that there can be no discrepancies in the standards used to assess groundwater risk resulting from percolation water soil contamination.

In the interest of avoiding inconsistencies in the determination of, and rationale for, insignificance thresholds, in groundwater contamination and risk assessments, and reclamation measure evaluation, the guide values for the soil-water exposure pathway should be harmonised with the values on the LAWA list."

At their 26th session in October 2000, the Senior Officials Conference endorsed *Geringfügigkeitsschwellen (Prüfwerte) zur Beurteilung von Grundwasserschäden und ihre Begründung* (Insignificance threshold values (guide values) for the assessment of groundwater pollution and the attendant determination methodologies) and asked LAWA to compile a list of insignificance thresholds for the assessment of groundwater contamination.

In response to this request, LAWA established a Permanent Committee on Groundwater and Water Management and a Subcommittee on Insignificance Thresholds.

The present report is based on the insignificance thresholds determination criteria that were elaborated by the subcommittee, as well as the relevant data from the professional literature. The report also contains the values and criteria that formed the basis for the determinations. The substances selected cover most of the parameters specified in Annex 2(3) (Prüfwerte für den Wirkungspfad Boden-Grundwasser ["Guidance values for the soil-groundwater exposure pathway"]) of the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV)), as well as other contaminated site and recycling related parameters, for all of which parameters sufficient data was available.

The present report and the data sheets thereof were accepted in September 2004 by the 127th general meeting of LAWA, the 83rd session of LAGA, and the 26th session of LABO. The Environmental Minister's Conference also approved publication of the report in 2004.

2 Determination of insignificance thresholds

2.1 Standards and principles

At its 35th session in June 2001, the LAWA Permanent Committee on Groundwater and Water Management decided to base the determination of insignificance threshold concentration levels on ecotoxicity and human toxicity factors. At its 29th meeting in May 2002, the Senior Officials Conference approved this procedure by adopting the document entitled "GAP-Papier" (LAWA 2002).

The committee defined "insignificance threshold" as any concentration level that (a) has no relevant ecotoxicity implications, even in the presence of substance concentrations exceeding regional background levels; and (b) is compliant with Drinking Water Ordinance requirements or parameters that are based on the Ordinance.

Hence, groundwater whose pollution levels are within the insignificance threshold

- is water that is fit for human consumption in any setting;

and

- still constitutes an intact biota, since (among other reasons) groundwater is an integral component of the ecosystem, and either forms the base flow for surface or impacts the characteristics of groundwater dependent wetlands.

Hence, insignificance thresholds are defined on the basis of ecotoxicity and human toxicity data that meet the following criteria:

– Statutory (and hence widely accepted) values were given priority over those derived from experts reports

– As a rule, data from individual published test reports was not used; instead, data sets that have been discussed and evaluated in the professional literature and are acknowledged were applied.

If there was a discrepancy between the values determined for potability and ecotoxicity, the lower value was used for the insignificance threshold value. If either human toxicity or ecotoxicity data was unavailable, the insignificance threshold determination was based on the available data set only.

Inasmuch as the relevant data sets in some cases can fall within very low concentration ranges, a lower limit was defined for these values in a subsequent step providing that they were not statutory values or values that are associated with a specific adverse effect.

2.2 Method for individual substances

2.2.1 Assessment in accordance with the Drinking Water Ordinance

Section 9 of the Drinking Water Ordinance (TrinkwV 2001, Bundesministerium für Gesundheit 2001) states that water whose threshold values exceed the limits mandated by the Ordinance can only be used as drinking water temporarily and subject to strict regulations. If the Ordinance threshold values meet either the empirical "safe for human consumption" criterion or falls into the "aesthetically acceptable drinking water quality" category, i.e. if these values are not based on water treatment or distribution processes, their application is prioritised and they are used intact for the insignificance threshold determination process.

If on the other hand the Ordinance threshold values are based on water treatment or distribution processes, or if values for relevant parameters are unavailable, assessments of aesthetic and health factors should be realised for each substance in accordance with the provisions of the Ordinance. Our human toxicity determinations were primarily based on published toxicological data (EIKMANN et al. 1999). If the Ordinance provided no relevant data, substance toxicity data was used instead, and was applied in accordance with the determination method for contaminated site assessment (UBA 1999). Data from other sources was applied as well, e.g. WHO Environmental Health Criteria monographs (http://www.who.int/peh-emf/publications/monographs/en/) and the EPA's IRIS Database for Risk Assessment (http://www.epa.gov/iris/). The various sources that were evaluated for individual human toxicity determinations are specified in the substance data sheets.

As a rule, it was estimated that the drinking water pathway accounts for 10 percent of the overall tolerable body dose of toxins (SCHELLSCHMIDT & DIETER 2000). This estimate was based on the assumption that substances that do not originate in the drinking water system, or pollutants that are not commonly found in such system, are mainly ingested through the food chain rather than the water supply. Up to 100 percent distribution quotients are admissible for substances that occur either commonly or naturally in the drinking water supply. The determination of the admissible concentrations of non-carcinogenic substances in water was based on daily intake of two liters of water and a body weight of 70 kg. For carcinogens, this determination should be based solely on post oral-ingestion cancer risk assessments that are regarded as being qualitatively appropriate. In addition, pursuant to the EU Drinking Water Directive, a supplementary lifespan risk amounting to $1 * 10^{-6}$ was used as a carcinogen risk level.

If the only carcinogen risk assessments available are deemed scientifically unsound by the Federal Environmental Agency (UBA), the insignificance threshold should be determined on the basis of the CEL_{min} (carcinogenic effect level) dose that was carcinogenic in 10 percent of animal models for their specified body dose. To realise this calculation, CEL_{min} is divided by 100.000 (in accordance with a supplementary 10^{-5} risk in 10 percent of the exposed animals ⇒ arithmetic supplementary lifespan risk, i.e. $1*10^{-6}$), and the result is then used as the acceptable lifelong body dose for determination of the insignificance threshold. In view of the heightened susceptibility of children to genotoxic carcinogens, a 5.87 supplementary risk was applied to the entirety of a mean 70 year lifespan for known high risk genotoxic carcinogens (DIETER AND HENSELING, 2003), except in cases where the Drinking Water Ordinance's insignificance threshold value for a substance of this type (benzene, benzo(a)pyrene and vinyl chloride) was used.

2.2.2 Ecotoxicity assessments

Insignificance thresholds are determined on the basis of ecotoxicity data from investigations of surface water organisms, a procedure that is adopted for the following reasons:

- No standard groundwater organism test method is available;
  and
- It is safe to assume that the sensitivity spectrum of surface water organisms provides a reasonably accurate characterization of groundwater organism biotas.

A Federal Environmental Agency study of specific pesticides (UBA 2001) showed that the products investigated induced ecotoxicogical effects in comparable concentration ranges for groundwater and surface water species, although adverse effects on the groundwater organisms are far longer lasting, and in some cases are essentially irreversible. No allowance should be made for this difference in applying ecotoxicity data for standard organisms to insignificance threshold determinations.

Surface water quality criteria are generally applicable to groundwater since surface water bodies are extensively fed by groundwater. This contention is also supported by Annex V(2.3.2) of the Water Framework Directive (WFD 2000), which states as follows: "The chemical composition of the groundwater body is such that the concentrations of pollutants (...) are not such as would result in failure to achieve the environmental objectives specified under Article 4 for associated surface waters..."

Ecotoxicity data is prioritised for insignificance threshold calculations in the following order:

1. Statutory environmental quality standards with documented ecotoxilogical implications for surface water biota are prioritised, and are applied "as is." These standards are primarily derived from Annex 5 (Umweltqualitätsnormen für die Einstufung des chemischen Zustands) of "Entwurf der LAWA-Musterverordnung zur Umsetzung der Anhänge II und V der WRRL" (LAWA 2003). Standards determined primarily on the basis of surface water background levels or suspended matter content are not applied.

2. Pursuant to the relevant statutory environmental standards, predicted no effect concentration (PNEC) values are accorded second-rank priority for purposes of insignificance threshold determination. This data is determined on the basis of the latest findings and in accordance with stringent, transparent and Community wide standards (Technical Guidance Document TGD2003), is reviewed by a battery of experts in accordance with EU chemical regulations, and is approved on submission of final risk assessment report (RAR 2002).
3. Inasmuch as LAWA targets were the starting point for the quality target debate in Germany, the data was incorporated into the relevant environmental quality standards. If neither an environmental quality standard nor a PNEC value is available for a substance, the LAWA targets should be used (LAWA 1997, LAWA 1998 a and b).
4. If neither of the aforementioned type of data is available, the insignificance thresholds are determined on the basis of MPC and MPA values from a Dutch report (Crommentuijn et al. 1997, de Bruijn et al., 1999). According to the Technical Guidance Document, the statistical extrapolation procedure that is used to calculate MPC and MPA values is an accredited PNEC determination method.

The determination criteria for the aforementioned data will now be summarised. For more detailed information, see the relevant literature (UBA 2000) which specifies all of the known water quality criteria, goals and standards.

Environmental quality standards

The first set of environmental quality standards for insignificance threshold data comprise individual substances and substance groups, as defined by Community environmental quality standards, as well as the priority substances defined by the WFD. These standards were adopted from Annex 5 of “Entwurf der LAWA-Musterverordnung zur Umsetzung der Anhänge II und V der WRRL” (LAWA 2003).

Likewise applied were the chemical quality components of the environmental quality standards that are used to define good and very good ecological water body status in accordance with Annex 4 of “LAWA-Musterverordnung,” insofar as the standards related to aquatic biota. These environmental quality standards were defined in accordance with Annex V(1.2.6) of the WFD (“Procedure for the setting of chemical quality standards by Member States”) or were based on LAWA targets. Hence in this case the criteria for insignificance threshold determination data were analogous to those used for the other data sources.

Also applied to insignificance threshold determination are the quality objectives laid down in Directive 76/464/EEC of 4 May 1976 (“Water pollution by discharges of certain dangerous substances”) and the daughter directives that were implemented by the German Laender in accordance with “Musterverordnung der LAWA” (LAWA 2000).

- PNEC (**P**redicted **N**o **E**ffect **C**oncentration) determination for aquatic biota

PNEC is realised for aquatic biota on the basis of the European system of risk assessment procedures for chemicals, in accordance with the relevant Technical Guidance Document (TGD 1996) and on the basis of long term monospecies investigations of representatives of three trophic stages, namely algae, small crabs (Entomostraca) and fish. The results of these investigations provide information on NOEC (**N**o **O**bserved **E**ffect **C**oncentration). The PNEC is determined on the basis of the lowest test results for the species most vulnerable to pollutants, divided by an equalization factor, which is 10 if all required data is available and increases if data is missing. This factor is used to compensate for the uncertainty resulting from the application to real water body conditions of individual laboratory test results based on relatively small numbers of organism species (as a rule, PNEC = the smallest NOEC divided by 10).

The added risk approach is also used for determination of insignificance thresholds, which means that the German basic value in accordance with Annex VIII of the Technical Guidance Document (see below) is added to the PNEC, which is based on the dissolved metal constituent.

Table 2.2-1: EU risk assessment reports on existing substances whose data was used to determine insignificance thresholds (Risk Assessment Reports in accordance with EEC 793/93 and EC 1488/94) (as at May 2004)

Substance	**CAS number**	**Priority list** number/ Member State in charge[1]	**EU existing substances reports** RAR = risk assessment report Env. = environmental assessment section HH = health assessment section
Boric acid (crude, natural)	10043-35-3	4./ A	No draft report is available
Boric acid	11113-50-1	4./ A	No draft report is available
Cadmium (Cd)	7440-43-9	3./ B	RAR **Final Draft**, July 2003 (Env. + HH)
Cadmium oxide	1306-19-0	3./ B	RAR **Final Draft**, July 2003 (Env. + HH)
Chromium trioxide (chrome VI)	1333-82-0	3./ UK	RAR **Draft**, November 2002 (Env. + HH)
Sodium chromate	7775-11-3	3./ UK	RAR **Draft**, November 2002 (Env. + HH)
Sodium dichromate	10588-01-9	3./ UK	RAR **Draft**, November 2002 (Env. + HH)
Potassium chromate	7778-50-9	3./ UK	RAR **Draft**, November 2002 (Env. + HH)
Ammonium dichromate	7789-09-5	3./ UK	RAR **Draft**, November 2002 (Env. + HH)
Fluoride RAR for hydrofluoric acid	7664-39-3	1./ NL	RAR **Final Report**, October 2001 (Env. + HH)
Naphthalene	91-20-3	1./ UK	RAR **Final Report**, 2003 (Env. + HH)
PER (tetrachlorethene)	127-18-4	1./ UK	RAR **Final Environment Report, August 2001**
TRI (trichlorethene)	79-01-6	1./ UK	**Final Report, September 2001** (Env.+HH)
Ethyl benzene	100-41-4	1. / D	Report not yet available
Styrole = vinyl benzene = ethenyl benzene	100-42-5	1. / UK	**Final Report, 2002** (Env.)
Benzene (monosubstance)	71-43-2	1./ D	**Draft** of 13.05.2002 (Env.)

Toluene	108-88-3	2. / DK	**Final Report, 2003** (Env. + HH)
Isopropyl benzene = cumene	98-82-8	1./ E	**Final Report, November 2001** (Env.+HH)
Phenol	108-95-2	1./ D	**Final Draft** of 11/2002 (Env.)
MTBE	1634-04-4	3./ FIN	**Final Report, 2002** (Env. + HH)
2,4-dinitrotoluene (2,4-DNT)	121-14-2	4./ E	Draft, May 2004
2-nitrotoluene (2-NT)	88-72-2	4./ E	Draft, May 2004
Substance	**CAS number**	**Priority list** number/Member State in charge[1]	**EU existing substances reports** RAR = risk assessment report Env. = environmental assessment section HH = health assessment section
Nitrobenzene	98-95-3	3./ D	No draft report is available
Diphenylamine	122-39-4	3. / D	No draft report is available
4--nonylphenol branched	84852-15-3	2./ UK	**RAR Final Report, 2002** (Env. + HH)
Nonylphenol	25154-52-3	2./ UK	**RAR Final Report, 2002** (Env. + HH)
1-propanol	71-23-8	2./ D	Draft of 19.08.2003
1,4-dichlorinated benzene	106-46-7	1./ F	**Final Report, May 2001** (Env.+HH)
1,2,4-trichlorinated benzene	120-82-1	2./ DK	**RAR Final Report, 2003** (Env. + HH)
Aniline = aminobenzene	62-53-3	1./ D	RAR Draft of 13.2.2002 (Env.+HH)
2-methoxyaniline = o-anisidine	90-04-0	2./ A	**RAR Final Report, 2002** (Env. + HH)
4,4'-methylendianiline = MDA	101-77-9	1./ D	**RAR Final Report, November 2001** (Env.+HH)
3,4-dichloraniline	95-76-1	1. / D	**RAR** of 18.7.2001 (Env.+HH)
dibutyl phthalate = DBP	84-74-2	1./ NL	**Final Report**, 2003 (Env. + HH)
Bisphenol A	80-05-7	3./ UK	RAR draft (Env.) 2/ 2002
Nickel	7440-02-0	3./ DK	Draft, May 2004
Zinc	7440-66-6	2./ NL	Draft, May 2004

[1.] A-Austria, B- Belgium, D – Germany, DK – Denmark, E – Spain, F – France, FIN – Finland, I – Italy, N – Norway, NL – The Netherlands, S – Sweden, UK – Britain

➢ <u>LAWA aquatic biota protection targets</u>

The targets in this domain are the same as for basic substance related ecotoxicity tests, but for representatives of four rather than three trophic phases. Tests are conducted on green algae, small crabs (Entomostraca), fish and – in the interest of testing groundwater self-purification capacities – bacteria as well. (The EU risk assessment procedure involves PNEC bacteria tests for wastewater treatment plants that are required neither for insignificance threshold value determination nor for sediment targets or PNEC.) Aquatic biota targets are determined on the basis of the lowest test results divided by a factor of 10, which is higher if ecotoxicity data is unavailable. These factors are slightly different from those mandated by the Technical Guidance Document.

In determining insignificance thresholds for groundwater, targets pertaining to surface water scenarios were excluded from consideration, particularly with regard to natural background concentrations or to substance concentrations resulting from the presence of suspended matter. The added risk approach was also applied, insofar as it was based on LAWA targets (see below).

➢ <u>MPC (**M**aximum **P**ermissible **C**oncentration), MPA (**M**aximum **P**ermissible **A**ddition)</u>

The frequency distribution for ecotoxicity test results relating to the substances investigated is determined on the basis of statistical extrapolation methods that were realised for risk assessment purposes. Biotope protection efficiency is determined on the basis of the data end point (NOEC, LC50) and the percentage of biotope species that are subject to protection. The MPC represents 95 percent protection efficiency for NOEC distribution. This means that the risk of aquatic system pollution is tolerable insofar as the exposure level for no more than 5 percent of the biotope species (i.e. 95 percent protection efficiency) exceeds the NOEC. In The Netherlands, a range of risk levels for the establishment of environmental quality standards has been developed in which the MPC constitutes the highest admissible risk level.

The MPC values for surface and ground water were collated and used for insignificance threshold value determination (Crommentuijn et al.1997, de Bruijn et al., 1999) since these risk values are readily comparable with PNEC values (UBA 2000). As was the case with PNEC determination, equalization factors were used if not enough data was available for a viable statistical analysis. Owing to the fact that no such analyses could be conducted due to a lack of data for all parameters, MPC groundwater values were computed on the basis of surface water values and in some cases groundwater specific background levels (Crommentuijn et al. 1997). In such cases, only MPA (**M**aximum **P**ermissible **A**ddition) values are adduced for purposes of insignificance thresholds determination, and the basic groundwater value for Germany is added to these values in accordance with the added risk approach.

In cases where the relevant values were unavailable in the data sources mentioned above, biotope quality criteria from other countries (see UBA 2000) was used instead.

In contrast to the procedure for organic substances, in assessing the risk induced by inorganic trace elements (particularly metals), it is necessary to allow for the fact that since these elements arise owing to geogenic factors, biotope organisms are in most cases exposed to minute amounts of these substances only, via a natural process. The naturally occurring trace element concentrations in the aquatic environment are subject to a timescale and these concentrations can fluctuate by several magnitudes. However, for the most part the organisms maintain a constant intracellular level of trace elements throughout this entire fluctuation range. In order to take the latter factor into account, and at the same time avoid classifying anthropogenically untainted groundwater as polluted when comparisons with insignificance thresholds are realised, specific basic values that characterise groundwater in Germany were added to the ecotoxicologically defined values in accordance with the added risk approach. These values were established via a LAWA research project that evaluated the findings of the various German Laender groundwater investigation programs (KUNKEL ET AL. 2004). Table 2.2-2 shows the basic values for inorganic trace elements and fluoride as the surface weighted mean of the 90th percentile value of 15 hydrogeological reference areas. The insignificance thresholds are obtained by adding the values shown in the table to the ecotoxicity PNEC for these elements (see sections on PNEC, LAWA targets, and MPC/MPA).

Table 2.2-2: Basic natural groundwater property values for inorganic trace elements and fluoride as the surface weighted mean of the 90th percentile value of 15 hydrogeological reference areas (KUNKEL ET AL. 2004)

Parameter	Surface weighted mean of the 90th percentile (in µg/l)	Parameter	Surface weighted mean of the 90th percentile (in µg/l)
Arsenic	2.6	Copper	10.1
Antimony	0.4	Molybdenum	(1.2)**
Barium	186	Nickel	12.6
Lead	3.9	Mercury	0.15
Boron	88	Selenium	1.6
Cadmium	0.3	Thallium	(<0.5)**
Chrome (total chrome)*	2.4	Vanadium	(1.6)**
Fluoride	270	Zinc	49.8
Cobalt	5.7		

*Chrome III for the most part

**Values from the states of Baden-Wurttemberg and Bavaria (not representative for Germany)

2.2.3 Plausibility tests of defined values

A lower limit is defined for substances that can not be definitively evaluated or whose insignificance thresholds *as computed* fall within very low concentration ranges.

The drinking water commission of the Ministry of Health has recommended that a so called health orientation value of 0.1 µg/L be used to evaluate drinking water substances for whose human toxicity no data or only insufficient data is available. Excluded from this category are "highly genotoxic substances," to which total lifelong ingestion of 0.01 µg/L apply (UBA 2003, Dieter 2003a).

Inasmuch as human ecotoxicity is often associated with relatively low contamination levels, and in order to ensure that (a) the often highly relevant ecotoxicity of specific substances is taken into account; and (b) the concentrations of these substances can be assayed, the lower insignificance threshold limit is defined as 0.01 µg/L in lieu of the drinking water commission's health orientation value of 0.01 µg/L. The foregoing does not apply to

- substances with demonstrable toxicity at levels below 0.01 µg/L; and
- substances that are subject to statutory EU quality targets amounting to less than 0.01 µg/L.

2.3 Method for organic substance groups

Insignificance thresholds are determined on the basis of ecotoxicity and human toxicity factors of individual substances. Chemically similar compounds that co-occur in the environment are often assessed in substance groups (e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl, PCB, and monoaromatic hydrocarbons (BTEX) including benzene and volatile halogenated hydrocarbons (VHH)). Inasmuch as the impact of the toxicity levels of such mixtures is difficult to predict owing to their differing compositions, it is necessary to define an upper composite parameter limit for these substance groups.

In calculating the values listed in Annex 2, allowance has to be made for the insignificance thresholds for individual substances (insofar as available) as well as their composite parameters, whose determination method is described in Annex 3 [see note on page 4].

3 Application rules for insignificance thresholds

Compliance with insignificance thresholds is documented via a comparison – *for each individual use case* – of determined or prognosticated substance concentrations and the applicable insignificance thresholds. Hence, cognate with Annex 2(3.2) of the Federal Soil Protection Ordinance (Bundesbodenschutzverordnung), which lays down application rules for insignificance thresholds, the provisions of current water legislation are concretised by specifying exactly which parameters apply to which use cases. For example, in some cases random samples of percolation water in natural or semi-natural soils (mainly topsoils) revealed higher concentrations of heavy metals than in groundwater. Hence, this factor must be taken into account when technical application rules are elaborated, and the toxicity value correction procedure must be modified using the basic values from the data on natural groundwater properties as a starting point. Any rules that are modified for special cases in this manner must be cleared with LAWA, insofar as the modification was not mandated by LAWA itself.

If geogenic groundwater background levels exceed the relevant insignificance thresholds, the competent authority can define "special case" values, in accordance with the determination criteria described in the present report (see Annex 1).

In the event of frequent instances of localised pollutant inputs and/or inputs that affect larger areas, water authorities should be provided with a management instrument that allows for the limitation of pollutant inputs in cases where also normal groundwater monitoring procedures detect irregularities. LAWA intends to elaborate a more explicit set of rules for this purpose.

Insignificance thresholds are not to be applied to the assessment of above-ground inputs such as atmospheric deposits or fertilisers. Nor are these values to be (mis)used as groundwater quality objectives, since they were intended for a wholly different purpose, namely as assessment benchmarks for localised pollutant inputs.

4 Notes on the Appendices

Annex 1 comprises a flowchart showing the procedure that is used to calculate insignificance thresholds. The insignificance thresholds that were determined for individual substances and composite parameters are shown in Annex 2. In the interest of clarity, the table in Annex 2 is divided into three parts that list the insignificance thresholds for inorganic substances (part 1), organic substances (part 2) and pesticides, biocides and explosive compounds (part 3).

Annex 3 (see note on page 4) contains the data sheets for the various substances and substance groups for which insignificance thresholds were determined. Each data sheet is prefaced by a tabular overview of information relating to insignificance thresholds, the available data, and the main determination criteria for the insignificance thresholds. An extensive exposition of insignificance threshold value determination methodology was dispensed with insofar as this methodology was clearly indicated by the criteria used in the datasheets. The methodology in such cases followed the general procedure described in section 2, in accordance with the literature cited in the relevant data sheet.

However, an extensive description of the methodology is necessary in cases where no such sources (e.g. TrinkwV) are available. In such cases, the data sheets provide a methodological description and the relevant citations. Basic values are indicated for inorganic trace elements only if non-statutory ecotoxicological insignificance thresholds were applied.

Annex 4 describes the determination methods that were used for the investigations of the substances and composite parameters mentioned in Annex 2. The lower application limit for some of the methods is greater than or equal to the relevant insignificance threshold value. In such cases, it is necessary to use non-standardised procedures, which must also be validated in accordance with the applicable determination method regulations.

Column 1 lists the substances and parameters that are to be investigated. Column 2 lists the analytic determination methods, virtually all of which are Deutsche Einheitsverfahren (DEV; Standard German procedures) that were for the most part incorporated into DIN standards or in some cases into EN or ISO standards. If two or more determination methods are indicated for one parameter, the most suitable method for each investigation can be selected, subject to the advisories in columns 3 and 4. Column 3 contains advisories regarding the methods that are to be used to calculate the various parameters. Column 4 provides information regarding lower application limits for the methods and the attendant units of measurement for reporting investigation results. In some cases the determination limit value can be higher (due to a mathematical matrix) than the tabular value. In addition, individual substance determination limits are governed by detectability and boundary conditions.

5 For further reading

Crommentuijn et al. 1997: Crommentuijn, T; Polder, MD; van de Plassche, EJ : Maximum permissible concentrations and negligible concentrations for metals, taking background concentrations into account. Report No. 601 501 001, National Institute of Public Health and the Environment, NL-Bilthoven, October 1997

de Bruijn et al. 1999 : J. de Bruijn, T. Crommentuijn, K. van Leeuwen, E. van de Plassche : Environmental risk limits in The Netherlands. National Institute of Public Health and Environment, RIVM-Report 601 640 001, NL-Bilthoven 1999

Dieter, HH 2003a: Kommentar zur Bewertung der Anwesenheit nicht oder nur teilbewertbarer Stoffe im Trinkwasser aus gesundheitlicher Sicht. Bundesgesundheitsbl. – Gesundheitsforsch. - Gesundheitsschutz 46(3), 245-248

Dieter, HH, Henseling, M. 2003: Kommentar zur Empfehlung: Maßnahmewerte (MW) für Stoffe im Trinkwasser während befristeter Grenzwert-Überschreitungen gem. § 9 para. 6-8 TrinkwV 2001. Bundesgesundheitsbl – Gesundheitsforsch – Gesundheitsschutz 46: 701-706, *including errata in 46: 915-916.*

EEC 1993: COUNCIL REGULATION (EEC) No 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances, Official Journal of the European Communities No. L 84

EC 1994: COMMISSION REGULATION (EC) No 1488/94 of 28 June 1994 laying down the principles for the assessment of risks to man and the environment of existing substances in accordance with Council Regulation (EEC) No 793/93, Official Journal of the European Communities No.L 161

The risk assessment carried out under Regulation 793/93 is conducted following the principles of the Regulation 1488/94 and following the detailed methodology laid down in the Technical Guidance Document on Risk Assessment for New and Existing Substances (TGD)

Eikmann et al. 1999: Eikmann Th., Heinrich U., Heinzow B., Konietzka R.: Gefährdungsabschätzung von Umweltschadstoffen ergänzbares Handbuch toxikologischer Basisdaten und ihre Bewertung, Erich Schmidt Verlag, Berlin, 1. Erg. Lfg. 12/99;

EUROPEAN CHEMICALS BUREAU under http://ecb.jrc.it last update: May 5, 2000 (risk assessment reports/existing substances)

Kunkel, R., Voigt, H.-J., Wendland, F. Hannappel, S. 2004: Die natürliche, ubiqitär überprägte Grundwasserbeschaffenheit in Deutschland, Schriften des Forschungszentrums Jülich, Reihe Umwelt Band 47

LAWA 1997: Zielvorgaben zum Schutz oberirdischer Binnengewässer, Band I: Teil I: Konzeption zur Ableitung von Zielvorgaben zum Schutz oberirdischer Binnengewässer vor gefährlichen Stoffen, Teil II: Erprobung der Zielvorgaben von 28 gefährlichen Wasserinhaltsstoffen in Fließgewässern. Länderarbeitsgemeinschaft Wasser, Berlin 1997

LAWA 1998: Geringfügigkeitsschwellen (Prüfwerte) zur Beurteilung von Grundwasserschäden und ihre Begründung. Bericht des ad-hoc-Arbeitskreises „Prüfwerte" der Länderarbeitsgemeinschaft Wasser (LAWA) vom 21. 12. 1998 (unpublished)

LAWA 1998a: Länderarbeitsgemeinschaft Wasser: Zielvorgaben zum Schutz oberirdischer Binnengewässer, Band II: Ableitung und Erprobung von Zielvorgaben zum Schutz oberirdischer Binnengewässer für die Schwermetalle Blei, Cadmium, Chrom, Kupfer, Nickel, Quecksilber und Zink. Berlin 1998

LAWA 1998b: Länderarbeitsgemeinschaft Wasser: Zielvorgaben zum Schutz oberirdischer Binnengewässer, Band III: Teil I: Konzeption zur Ableitung von Zielvorgaben zum Schutz oberirdischer Binnengewässer vor gefährlichen Stoffen, Teil II: Erprobung der Zielvorgaben für Wirkstoffe in Bioziden und Pflanzenbehandlungsmitteln für trinkwasserrelevante oberirdische Binnengewässer. Berlin 1998.

LAWA 2000: Musterverordnung über Qualitätsziele für bestimmte gefährliche Stoffe und zur Verringerung der Gewässerverschmutzung durch Programme. Umsetzung der Richtlinie 76/464/EWG vom 4.5.1976 in deutsches Recht, TOP 3.7 der 115. LAWA-Sitzung am 7.-8.9.2000 in Rostock

LAWA 2002(GAP-Papier): „ Principles of pre-emptive groundwater protection with waste recycling and the use of products" Länderarbeitsgemeinschaft Wasser, May 2002

LAWA 2003: „Musterverordnung zur Umsetzung der Anhänge II und V der Richtlinie 2000/60/EG des Europäischen Parlaments und des Rates vom 23. Oktober 2000 zur Schaffung eines Ordnungsrahmens für Maßnahmen der Gemeinschaft im Bereich der Wasserpolitik", Länderarbeitsgemeinschaft Wasser, Entwurf Stand 2.7.2003

RAR 2002: Risk Assessment Report pursuant to EEC 793/93 and EC 1488/94, researched in 2002 via European Chemicals Bureau and augmented where necessary using information from the Federal Environmental Agency in Berlin

Schellschmidt, B. & Dieter, HH. Gesundheitlich duldbare Höchstkonzentrationen für die Kontamination von Trinkwasser durch Pflanzenschutzmittel (Gesundheitliche Leitwerte), Gesundheitsbl – Gesundheitsforsch - Gesundheitsschutz 43(7): 494-504.

TGD2003: Technical Guidance Document on Risk Assessment for New and Existing Substances, siehe EC 1994 (http://ecb.jrc.it/)

TrinkwV 2001: Verordnung zur Novellierung der Trinkwasserverordnung vom 21. Mai 2001. Bundesgesetzblatt Teil I Nr. 24, 959 ff

UBA 1994: Zielvorgaben für gefährliche Stoffe in Oberflächengewässern. Bearbeitet von Gottschalk, Ch.; UBA-Texte 44/94, Umweltbundesamt, Berlin; cited in UBA 2000

UBA 1999: Berechnung von Prüfwerten zur Bewertung von Altlasten: Ableitung und Berechnung von Prüfwerten der Bundes-Bodenschutz- und Altlastenverordnung für den Wirkungspfad Boden - Mensch aufgrund der Bekanntmachung der Ableitungsmethoden und -maßstäbe im Bundesanzeiger Nr. 161a vom 28. August 1999. Edited by the Federal Environmental Agency. Contributors: Bachmann G, Oltmanns J, Konietzka R, Schneider K., Erich Schmidt Verlag, Berlin

UBA 2000: Umweltqualitätsziele für gefährliche Stoffe in Gewässern - Internationaler Vergleich der Ableitungsmethoden. Bearbeitet von Schudoma, D.; UBA-Texte 24/00. Umweltbundesamt, Berlin

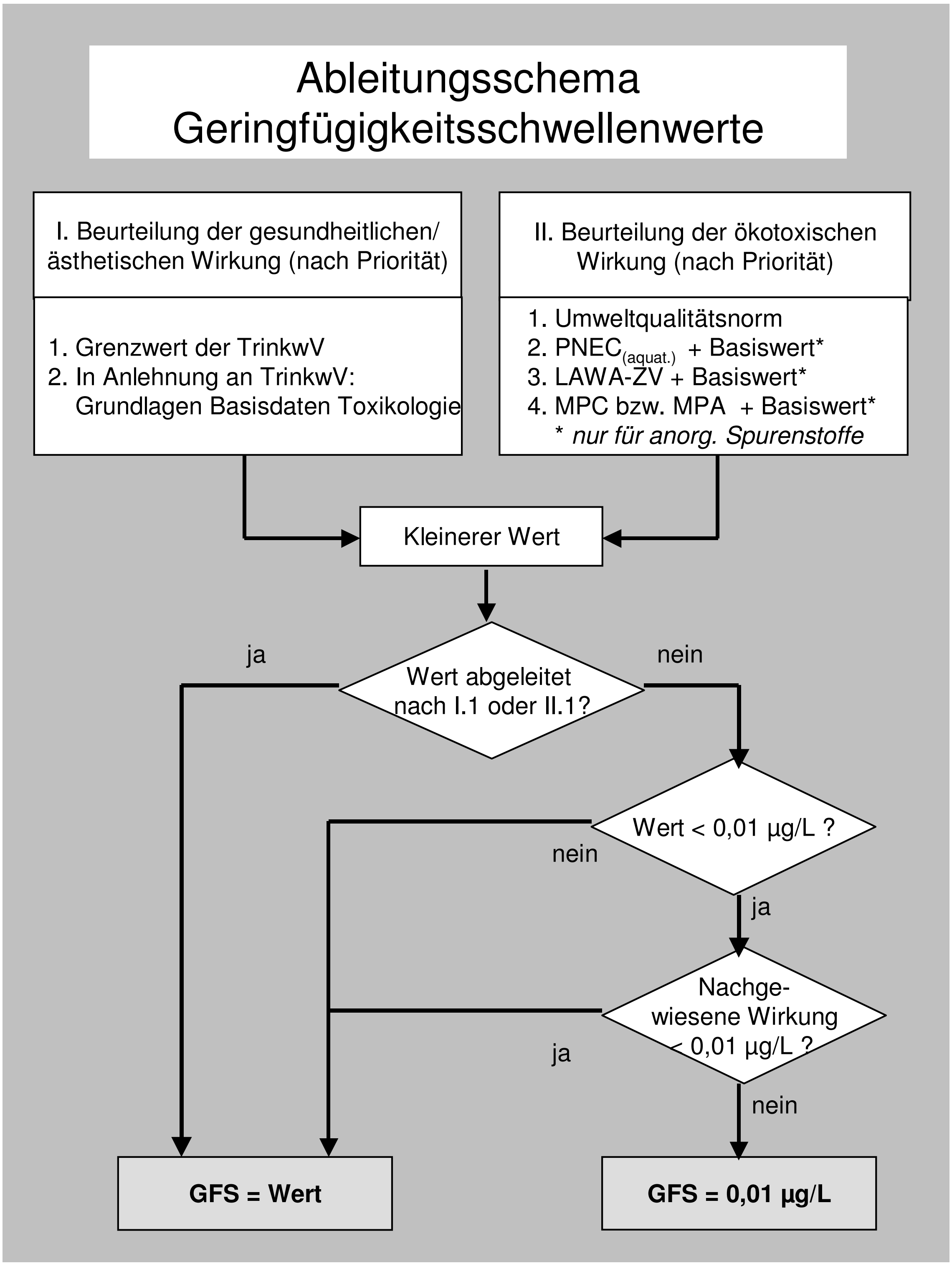
UBA 2001: Forschungsvorhaben FKZ: 298 28 415 „Ökotoxikologische Prüfung von Pflanzenschutzmitteln hinsichtlich ihres Potentials zur Grundwassergefährdung"; Realised by: Institut für Umweltchemie und Toxikologie der Fraunhofer Gesellschaft, Schmallenberg, UBA- TEXTE 76/01, Umweltbundesamt Berlin

UBA 2003: Bewertung der Anwesenheit teil- oder nicht bewertbarer Stoffe im Trinkwasser aus gesundheitlicher Sicht – Empfehlung der Trinkwasserkommission des Umweltbundesamtes. Bundesgesundheitsbl- Gesundheitsforsch- Gesundheitsschutz 46 (3): 249 - 251

WFD 2000: Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Communities no. L 321 of 22 December 2000 p.1

Annex 1: Methodology flowchart for the determination of insignificance thresholds

[Legende zur Abbildung:] Ableitungsschema... = Methodology flowchart for the determination of insignificance thresholds. | **Left column**: I. Assessment of health and aesthetic factors (according to priority) | 1. Threshold value pursuant to TrinkwV. | 2. Based on basic toxicity data pursuant to TrinkwV. | **Right column:** II. Ecotoxicity assessment (according to priority). | 1. Environmental quality standard. | 2. PNEC (aquatic) + basic value*. | 3. LAWA targets + basic value*. | 4. MPC or MPA + basic value*| nur... Applies to inorganic trace elements only. | Kleinerer = Lower value. | Wert... Value determined on the basis of 1.1 or II.1? | ja = Yes. | Nein = No. | Wert... = Value < 0.01 µg/L? | Nach... = Documented effect with < 0.01 µg/L? | *GFS = Wert* = Insignificance threshold value = value | GFS... = Insignificance threshold value = 0.01 µg/L


Ableitungsschema
Geringfügigkeitsschwellenwerte
I. Beurteilung der gesundheitlichen/ ästhetischen Wirkung (nach Priorität)
1. Grenzwert der TrinkwV
2. In Anlehnung an TrinkwV: Grundlagen Basisdaten Toxikologie
II. Beurteilung der ökotoxischen Wirkung (nach Priorität)
1. Umweltqualitätsnorm
2. PNEC(aquat.) + Basiswert*
3. LAWA-ZV + Basiswert*
4. MPC bzw. MPA + Basiswert*
* nur für anorg. Spurenstoffe
Kleinerer Wert
ja
nein
Wert abgeleitet nach I.1 oder II.1?
Wert < 0,01 µg/L ?
nein
ja
Nachge- wiesene Wirkung < 0,01 µg/L ?
ja
nein
GFS = Wert
GFS = 0,01 µg/L

Annex 2: Insignificance thresholds for the assessment of localised groundwater pollution

Part 1: Inorganic parameters

Inorganic parameters	Insignificance thresholds (in µg/L)
Antimony (Sb)	5
Arsenic (As)	10
Barium (Ba)	340
Lead (Pb)	7
Boron (B)	740
Cadmium (Cd)	0.5
Chrome (CR III)	7 (see Annex 3)
Cobalt (Co)	8
Copper (Cu)	14
Molybdenum (Mo)	35
Nickel (Ni)	14
Mercury (Hg)	0.2
Selenium (Se)	7
Thallium 1(Tl)	0.8
Vanadium (V)[1]	4
Zinc (Zn)	58
Chloride (Cl^-)	250 mg/L
Cyanide (CN^-)	5 (50) (see Annex 3)
Fluoride (F^-)	750
Sulfate (SO_4^{2-})	240 mg/L

1) Application of the insignificance threshold for vanadium has been suspended until December 31, 2007. Although the value reflects the latest findings on vanadium's human toxicity and lifelong protection against this substance, it is based on incomplete data whose significance is a matter of controversy. The suspension was instituted mainly in order to give manufacturers the opportunity to gather additional experimental data on ecotoxicity and human toxicity. It is safe to assume that the availability of higher quality data will result in a higher insignificance threshold value for vanadium.

Annex 2: Insignificance thresholds for the assessment of localised groundwater pollution

Part 2: Organic parameters

Organic parameters	**Insignificance thresholds (in µg/L)**
Σ Polycyclic aromatic hydrocarbons (PAHs)[1]	0.2
Anthracene, benzo[a]pyrene, dibenz(a,h)anthracene	0.01 each
Benzo[b]fluoranthene, benzo[k]- fluoranthene, benzo[ghi])perylene,fluoranthene, indeno(123-cd)pyrene	0.025 each
∑ naphthaline and methylnaphthaline	1
∑ Volatile halogenated hydrocarbons (VHH)[2]	20
∑ Trichlorathene and tetrachlorethene	10
1,2 dichlorethane	2
Chlorethene (vinyl chloride)	0.5
∑ PCB[3]	0.01
Hydrocarbons[4]	100
∑ Alkalised benzene	20
Benzene	1
MTBE	15
Phenol[5]	8
Nonylphenol	0.3
∑ Chlorinated phenol	1
Hexachlorobenzene	0.01
∑ Chlorinated benzene	1
Epichlorhydrin	0.1

1) Total PAHs: The total of all PAHs excluding naphthalene and methylnaphthalene, generally determined via the total of the 15 substances on the EPA list, excluding naphthalene, and in some cases also taking into account other relevant PAHs, e.g. aromatic heterocyclenes such as chinoline.
2) Total VHH: The total of all volatile halogenated C_1 and C_2-hydrocarbons including trihalogen methane. Compliance with the insignificance thresholds for trichlorothene, tetrachlorothene, chlorothene is also required by law.
3) Total polychlorinated biphenyl, which is generally determined on the basis of the six Ballschmiter substances in accordance with DIN 51527, multiplied by five; and in some cases (e.g. for known substance spectrums) solely on the basis of the total values of all relevant substances in accordance with DIN 38407-F3.
4) Determined in accordance with DEV H53. ISO 9377-1 gravimetry can be used for higher concentrations. For gas chromatography analyses, the tabular value pertains to total hydrocarbon ranging from C_{10} to C_{40}.
5) Inasmuch as no standardised procedure is currently available whose lower application limit is less than or equal to the insignificance threshold, it is necessary to use a non-standardised procedure, which must also be validated in accordance with the applicable determination method regulations. Generally a phenol index determination procedure is realised. If the findings are positive, a calculation is to be realised for the relevant individual substances.

Annex 2: Insignificance thresholds for the assessment of localised groundwater pollution

Part 3: Pesticides, biocides and explosive compounds

Pesticides and biocides	*Insignificance threshold value (in µg/L)*	*Explosive compounds*	*Insignificance threshold value (in µg/L)*
∑ Pesticides and biocides	0.5	**Nitropenta (PETN)**	10
Individual pesticides	0.1 each	**2-nitrotoluene**	1
Aldrine, azinphos-methyl, dichlorvos, dieldrin, endosulfane, etrimfos, fenitrothion, fenthion, parathion-ethyl	0.01 each	**3-nitrotoluene**	10
Chlordane	0.003	**4-nitrotoluene**	3
Disulfoton	0.004	**2-amino-4,6-dinitrotoluene**	0.2
Diuron	0.05	**4-amino-2,6-dinitrotoluene**	0.2
Hexazinon	0.07	**2,4-dinitrotoluene**	0.05
Malathion, parathion-methyl	0.02 each	**2.6-dinitrotoluene**	0.05
Mevinphos	0.0002	**2,4,6-trinitrotoluol**	0.2
Pentachlorphenol	0.1	**Hexogen**	1
Phoxim	0.008	**2,4,6-trinitrophenol (picric acid)**	0.2
Triazophos, trifluralin, heptachlor, heptachlorepoxide	0.03 each	**Nitrobenzene**	0.7
Tributyl tin[1]	0.0001	**1,3,5-trinitrobenzene**	100
Trichlorphon	0.002	**1,3-dinitrobenzene**	0.3
Triphenyl tin and dibutyl tin compounds	0.01	**hexanitrodiphenylamin (hexyl)**	2
		Tetryl	5
		Octogen	175

[1]Inasmuch as no standardised procedure is currently available whose lower application limit is less than or equal to the insignificance threshold value, it is necessary to use a non-standardised procedure, which must also be validated in accordance with the applicable determination method regulations.

Annex 4: Determination methods and lower application limits

Part 1: Metal ions, semi-metal ions and other cations and anions

Parameter	Determination method	Method type	Lower application limit[1]
Antimony (Sb)	DIN 38405-32-2 DIN 38405-32-1 DIN EN ISO 11885 DIN 38406-29	AAS (hydride) Graphite tube/AAS ICP-OES ICP-MS	0.001 mg/L 0.002 mg/L 0.1 mg/L 0.001 mg/L
Arsenic (As)	DIN EN ISO 11969 DIN EN ISO 11885 DIN 38406-29	AAS (hydride) ICP-OES ICP-MS	0.001 mg/L 0.1 mg/L 0.001 mg/L
Barium (Ba)	DIN EN ISO 11885 DIN 38406-28 analogous to DIN EN ISO 5961 DIN 38406-29	ICP-OES Flames/AAS Graphite tube/AAS ICP-MS	0.01 mg/L 0.1 mg/L 0.5 mg/L 0.0005 mg/L
Lead (Pb)	DIN 38406-6-1 DIN 38406-6-2 DIN EN ISO 11885 DIN 38406-29	Flames/AAS Graphite tube/AAS ICP-OES ICP-MS	0.5 mg/L 2 mg/L 0.1 mg/L 0.0002 mg/L
Boron (B)	DIN EN ISO 11885 DIN 38405-17 DIN 38406-29	ICP-OES Spectral photometry ICP-MS	0.05 mg/L 0.05 mg/L 0.01 mg/L
Cadmium (Cd)	DIN EN ISO 5961-HA2 DIN EN ISO 5961-HA3 DIN EN ISO 11885 DIN 38406-29	Flames/AAS Graphite tube/AAS ICP-OES ICP-MS	0.05 mg/L 0.0003 mg/L 0.01 mg/L 0.0005 mg/L
Total chrome (Cr, total chrome(Cr III)	DIN EN 1233-HA3 DIN EN 1233-HA4 DIN EN ISO 11885 DIN 38406-29	Flames/AAS Graphite tube/AAS ICP-OES ICP-MS	0.5 mg/L 2 mg/L 0.01 mg/L 0.001 mg/L
Chromate (Cr VI)[2, 3]	DIN 38405-24 DIN EN ISO 10304-3	Spectral photometry Ion chromatography	0.05 mg/L 0.05 mg/L
Cobalt (Co)	DIN 38406-24-1 DIN 38406-24-2 DIN EN ISO 11885 DIN 38406-29	Flames/AAS Graphite tube/AAS ICP-OES ICP-MS	0.2 mg/L 2 mg/L 0.01 mg/L 0.0002 mg/L
Copper (Cu)	DIN 38406-7-1 DIN 38406-7-2 DIN EN ISO 11885	Flames/AAS Graphite tube/AAS ICP-OES	0.1 mg/L 2 mg/L 0.01 mg/L

	DIN 38406-29	ICP-MS	0.001 mg/L
Molybdenum (Mo)	analogous to DIN EN ISO 5961 DIN EN ISO 11885 DIN 38406-29	Graphite tube/AAS ICP-OES ICP-MS	0.001 mg/L 0.03 mg/L 0.0003 mg/L
Nickel (Ni)	DIN 38406-11-1 DIN 38406-11-2 DIN EN ISO 11885 DIN 38406-29	Flames/AAS Graphite tube/AAS ICP-OES ICP-MS	0.2 mg/L 5 mg/L 2 mg/L 0.001 mg/L
Mercury (Hg)	DIN EN 1483 DIN EN 12383	Cold vapor/AAS Cold vapor/AAS (following amalgam enrichment)	0.0001 mg/L 0.00001 mg/L
Selenium (Se)	DIN 38405-23-2 DIN 38405-23-1 DIN EN ISO 11885 DIN 38406-29	AAS (hydride) Graphite tube/AAS ICP-OES ICP-MS	0.001 mg/L 5 mg/L 0.1 mg/L 0.01 mg/L
Thallium 1(Tl)	DIN 38406-26 DIN EN ISO 11885 DIN 38406-29	Graphite tube/AAS ICP-OES ICP-MS	5 mg/L 0.1 mg/L 0.001 mg/L
Vanadium (V)	DIN EN ISO 11885 DIN 38406-29	ICP-OES ICP-MS	0.01 mg/L 0.001 mg/L
Zinc (Zn)	E DIN 38406-8 DIN EN ISO 11885 DIN 38406-29	Flames/AAS ICP-OES ICP-MS	0.05 mg/L 0.01 mg/L 0.001 mg/L
Chloride (Cl^-)	DIN 38405-1 DIN EN ISO 10304-1 DIN EN ISO 10304-4 DIN EN ISO 15682	Photometry Ion chromatography Ion chromatography Flow analysis	10 mg/L 0.1 mg/L 0.1 mg/L 1 mg/L
Total cyanide (total CN^-)	DIN 38405-13-1, DIN 38405-14-1 DIN EN ISO 14403	Spectral photometry Flow analysis	0.02 mg/L 0.02 mg/L
Voltatile cyanide (CN^-)	DIN 38405-13-2, DIN 38405-14-2 DIN EN ISO 14403	Spectral photometry Flow analysis	0.02 mg/L 0.02 mg/L
Fluoride (F^-)	DIN EN ISO 10304-1/-2 DIN 38405-4-1 DIN 38405-4-2	Ion chromatography Fluoride ion selection. Electrode determination following hydrolysis and distillation	0.1 mg/L 0.1 mg/L 0.2 mg/L
Sulfate (SO_4^{2-})	DIN 38405-5 DIN EN ISO 10304-1	Gravimetry Ion chromatography	20 mg/L 0.1 mg/L

Annex 4: Determination methods and lower application limits

Part 2: Organic substances and substance groups

Parameter	**Determination method**	**Method type**	**Lower application limit**[1]
Polycyclic aromatic hydrocarbons (PAHs)[4]	DIN 38407-18 ISO FDIS 17993 DIN 38407-7-1[5] (screening) DIN 38407-7-2[5] DIN 38409-13-2[5] (screening)	Hexane extraction, HPLC-FLD Hexane extraction, HPLC-FLD HPTLC HPTLC HPLTC	0.005-0.01 µg/L 0.005-0.01 µg/L 0.04 µg/L
VHH	DIN EN ISO 10301 (F 4) DIN EN ISO 15680	Pentane extraction, GC-ECD Headspace, GC-ECD, purge and trap, GC-ECD or GC-MS	0.01-50 µg/L 0.1-200 µg/L 0.01-1 µg/L
Chlorethene (vinyl chloride)	DIN 38413-2 DIN EN ISO 15680	GC-FID Purge and trap, GC-ECD or GC-MS	5 µg/L 0.02 µg/L
PCB	DIN 38407-2 DIN EN ISO 6468 (F 1) DIN 38407-3-1 (indicator substance.) DIN 38407-3-2 (peak pattern) DIN 38407-3-3	Fluid extraction, GC-ECD Fluid extraction, GC-ECD Hexane extraction, GC-ECD Hexane extraction , GC-ECD Hexane extraction, GC-MS	0.001-0.01 µg/L 0.001-0.01 µg/L 0.001 µg/l - 0.01-0.1µg/L
Hydrocarbons[6]	DIN EN ISO 9377-2 Overview analysis	Extraciton using aceteone/naphta/GC-FID Fingerprint identification: GC-FID without quantification	0.1 mg/L
Alkalised benzene (BTEX)	ISO 11423-1 DIN 38407-9-1 ISO 11423-2 DIN 38407-9-2 E DIN EN ISO 15680	Steam chamber, GC-FID Steam chamber, GC-FID Pentane extraction, GC-FID Pentane extraction, GC-FID Purge and trap, GC-ECD or GC-MS	5 µg/L 5 µg/L 5 µg/L 5 µg/L 0.02–0.05 µg/L
MTBE	DIN EN ISO 15680 (must be validated for MTBE) DIN 38 407-9	Purge and trap, GC-FID or GC-MS Steam chamber, GC-MS	0.05 µg/L 1 µg/L
Phenols[2] - monovalente phenoles[7]	 (E) ISO 8165-1 (E) ISO 8165-2 analogous to DIN EN 12673 (F 15)	 Fluid extraction, GC-FID or GC-ECD Derivatization, GC-ECD Derivatization, GC-MS	 0.1 µg/L 0.1 µg/L 0.1 µg/L

- Phenol index[8]	 DIN 38409-16-2 DIN EN ISO 14402 (H 37)	Spectral photometry Flow analysis	10 µg/L 10 µg/L
Nonylphenols	ISO /18857-1	Fluid extraction, GC-MS	0.02 µg/L
Chlorinated phenols	DIN EN 12673 (F 15)	Extractive derivatization using acetane hydride/GC-ECD	0.1 µg/L
Chlorbenzene – Cl_1-Cl_3-chlorbenzene – Cl_3-Cl_6-chlorbenzene	 EN ISO 10301 (F 4) DIN EN ISO 6468 (F 1) DIN 38407-2	 Headspace, GC-ECD Fluid extraction, GC-ECD Fluid extraction, GC-ECD	 0.2-0.5 µg/L 0.001-0.01 µg/L 0.001-0.01 µg/L
Epichlorhydrin	DIN EN 14207 (P 9)	Solid phase extraction, GC-MS	0.1 µg/L
Pesticides and biocides -Volatile hydrocarbon organochlorinated pesticide[9] - Organic N and P compounds[10] - Phenoxy carbonic acid herbicide PSM (selection)	 DIN EN ISO 6468 (F 1) DIN 38407-2 DIN EN ISO 10695 (F 6) DIN EN ISO 11369 (F 12) DIN 38407-14, DIN ISO 15913 (F 20) DIN V 38407-11	 Fluid extraction, GC-ECD (GC-MS in some cases as well) Fluid extraction, GC-PND Solid phase extraction, GC-PND Solid phase extraction, HPLC-UV-DAD Solid phase extraction, GC-MS Solid phase extraction, GC-MS Solid phase extraction, HPTLC-AMD	 0.001-0.01µg/L 0.1 – 1µg/L 0.051 – 0. 061µg/L 0.025 – 0.1µg/L 0.05 µg/L 0.05 µg/L 0.05 µg/L
Organic tin compounds	DIN 38407-13	Hexane extraction; GC/MS, GC/FPD, or GC/AED	0.01 µg/L
Nitropenta (PETN)	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
2-nitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction., HPLC-UV-DAD Toluene extraction or solid	0.1 - 0.5 µg/L 0.05 µg/L
3-nitrotoluene	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
4-nitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase	0.1 - 0.5 µg/L 0.05 µg/L
2-amino-4,6-dinitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase	0.1 - 0.5 µg/L 0.05 µg/L
4-amino-2,6-dinitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase extraction, GC/MS	0.1 - 0.5 µg/L 0.05 µg/L

2,4-dinitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase extraction, GC/MS	0.1 - 0.5 µg/L 0.05 µg/L
2,6-dinitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase extraction, GC/MS	0.1 - 0.5 µg/L 0.05 µg/L
2,4,6-trinitrotoluene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase extraction, GC/MS	0.1 - 0.5 µg/L 0.05 µg/L
Hexogen	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
2,4,6-trinitrophenol (picrin acid)	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
Nitrobenzene	DIN 38407-17	Toluene or solid phase extraction, GC/MS	0.05 µg/L
1,3,5-trinitrobenzene	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
1,3-dinitrobenzene	DIN 38407-21 DIN 38407-17	Solid phase extraction, HPLC-UV-DAD Toluene or solid phase extraction, GC/MS	0.1 - 0.5 µg/L 0.05 µg/L
Hexanitrodiphenylamin (Hexyl)	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
Tetryl	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L
Octogen	DIN 38407-21	Solid phase extraction, HPLC-UV-DAD	0.1 - 0.5 µg/L

1) The lower application limits, which are substance and matrix dependent, probably have to be corrected upwards for contaminated sites.

2) Inasmuch as no standardised procedure is available that would allow for achievement or falling short of the insignificance threshold, a non-standardised procedure must be used. This procedure must also be validated in accordance with the applicable analysis procedure regulations, and the procedure is to be described.

3) Consequently, chromate determination should be realised using atomic spectrography following chromatographic isolation of chrome (III).

4) In the event of positive findings in the selection test (results > 50 ng/l) using a method such as thin layer chromatography in accordance with DIN 38409-13-2, or if the presence of the substance is suspected for other reasons, specimen extracts are to be investigated at baseline and during the testing period for purposes of identifying (a) technical products containing PAHs; and (b) other industry specific parameters, in both cases via GC-MS screening. The investigation results are to form the basis for determining the method for routine measurements.

5) Four PAHs each, in accordance with the Drinking Water Ordinance (Trinkwasserverordung).

6) The hydrocarbon index is to be determined using DIN EN ISO 9377-2 compliant gas chromatography, which allows for cumulative assessments and for identification of individual substances, and for determination of the type of technical product. If individual signals occur in the chromatogram that are usually not observed in petroleum mixtures, iterative cleaning with florisil is to be realised with a view to determining whether the signals are generated by a hydrocarbon. If hydrocarbon signals are detected, the signal intensities must maintain the same ratio to the other hydrocarbons. If the signals taper off proportionally, the florisil cleaning is to be realised iteratively if necessary. Concentrations exceeding 50 mg/L can be quantified gravimetrically in accordance with E DIN EN ISO 9377-1, whereby negative findings resulting from vaporization of the low-boiling component must also be taken into account. This method can also be used for the quantification of high boiling hydrocarbon > C_{40}.

7) Selected monovalent phenoles.

8) If the insignificance threshold for the phenol index is exceeded (see table 3.1.-1), a determination is to be realised for each substance.

9) e.g. aldrin, DDT, HCH mixtures.

10) Selected organic N and P compounds such as triazine herbicides, phenyl urea herbicides, and organic phosphoric acid derivatives.