Common Implementation Strategy for the Water Framework Directive

Environmental Quality Standards (EQS)

Substance Data Sheet

Priority Substance No. 3

Atrazine

CAS-No. 1912-24-9

Final version
Brussels, 15 January 2005

Disclaimer

This data sheet provides background information on the setting of the Environmental Quality Standard in accordance with Article 16 of the Water Framework Directive (2000/60/EC). The information was compiled, evaluated and used as outlined in the Manual [4] and has been discussed in a consultative process with the Expert Advisory Forum on Priority Substances and the Expert Group on Quality Standards. Furthermore, it has been peer-reviewed by the SCTEE[11]. The substance data sheet may, however, not necessarily represent the views of the European Commission.

New upcoming information was considered and included up to the date of finalisation of this data sheet. Information becoming available after finalisation of this document will be evaluated in the review process of priority substances according to Art. 16(4) of the Water Framework Directive. If necessary, the Environmental Quality Standard substance data sheets will then be revised in the light of technical and scientific progress.

1 Identity of substance

Priority Substance No: 3	Atrazine
CAS-Number:	1912-24-9
Classification WFD Priority List *:	WFD_PSR

* PS: priority substance; PHS: priority hazardous substance; PSR: priority substance under review according to Decision 2455/2001.

2 Proposed quality standards

2.1 Overall quality standards

Ecosystem	**Quality Standard**	**Comment:**
AA-QS all surface waters covered by the WFD	0.6 µg/l	Overall QS refers to the protection of the pelagic communities, see 8.1 & 8.6
MAC-QS	2.0 µg/l	see section 8.1

2.2 Specific quality standards

Protection Objective #	**Quality Standard**	**Comment:**
Pelagic community all types of surface water covered by the WFD	0.6 µg/l	see section 8.1
Benthic community all types of sediments covered by the WFD	1.12 µg/kg (wet wt) 5.2 µg/kg (dry wt)	tentative standard (EP method) based on MAC-QS; see section 8.2
Predators (secondary poisoning)	derivation of QS not required	trigger values not met see section 8.3
Food uptake by man	derivation of QS not required	trigger values not met see section 8.4
Abstraction of water intended for human consumption (AWIHC)	< 1 µg/l	A1-value for Σpesticides in CD 75/440/EEC; see section 8.5
Water intended for human consumption (WIHC)	0.1 µg/l	Drinking water standard set in CD 98/83/EC

If justified by substance properties or data available, QS for the different protection objectives are given independently for freshwater environments, transitional waters or coastal and territorial waters

3 Classification

R-Phrases and Labelling	**Reference:**
Xn; R48/22 - R43 - N; R50-53	[12]
Proposal of rapporteur: Xn, Xi, N; R: 40-43-48-50/53	[1]

4 Physical and chemical properties

Property	**Value:**	**Ref.**
Vapour pressure		
Henry's law constant	1.5×10^{-4} Pa m³/mol	[1]
Solubility in water	low solubility in water	[1]
Dissociation constant	1.6, becoming protonated at pH < 1.6	[1]

5 Environmental fate and partitioning

Property	**Value:**	**Ref.**
Hydrolytic stability (DT_{50})	Atrazine does not hydrolyse at environmentally occurring pHs or temperatures	[1]
Photostability (DT_{50}) (aqueous, sunlight, state pH)	extent of photolytic degradation is unclear, a test in natural sunlight resulted in little degradation	[1]
Readily biodegradable (yes/no)	not readily degradable in aquatic systems	[1]
Degradation in Water/sediment -DT_{50} water - DT_{50} whole system	28-134 d	[1]
Mineralization		
Bound residue		
Distribution in water / sediment systems (active substance)	In aerobic natural sediment water systems, experiments conducted in the dark showed very slow removal of atrazine from the water phase (half life 28-134) days and even slower removal in anaerobic conditions. This loss is mainly via partitioning into the sediment (and then to bound residues)... From the fate and behaviour data assessed in Section B.7.4, it can be estimated that **20-30% of applied atrazine will partition into the sediment** after 7-28 days. Therefore, **atrazine entering surface waters may pose a risk to sediment dwelling invertebrates**.	[1]
Distribution in water / sediment systems (metabolites)		
Residues relevant to the aquatic environment	Hydroxyatrazine appears to be the predominant metabolite from all routes of breakdown in water with lesser amounts of deethylatrazine and deisopropylatrazine formed. None of these are considered to be environmentally relevant	[1]
Partition co-efficient (log P_{OW}) Koc	2.5 86	[1] [1]
BCF (fish)	7.7 (fillet) 15 (viscera) 12 (whole fish)	[1]

6 Effect data (aquatic environment)

For atrazine, a risk assessment monograph in line with the provisions of Council Directive 91/414/EEC (placing of plant protection products on the market) is available [1]. However this report was finalized in 1996 and does not consider data that became available in the meantime. In order to make best use of all effect data available at present for the derivation of a water quality standard, it was therefore agreed at the workshop of the Expert Group on Quality Standards (12-16 May 2003, Brussels) that the United Kingdom in its competence as Rapporteur Member State for atrazine shall perform an assessment of aquatic effect data that became available after finalisation of the monograph. It was further concluded that an attempt should be made to derive a quality standard proposal by means of statistical extrapolation (e.g. the species sensitivity distribution method) and compare the outcome of this approach with the standard assessment factor method.

Consequently, the UK Environment Agency has provided in October 2003 a "Report on Quality Standards for Atrazine and Simazine under the Water Framework Directive" [5]. This report analyses different data on atrazine to determine long-term quality standards (AA-QS). Data sources used to produce a consolidated list of studies were the Alterra database[1] for atrazine, data provided by the Fraunhofer-Insitiute (forwarded to FHI for the purpose of QS-setting by the United Kingdom, the Netherlands, France and Germany), data on endocrine disruption studies published by Solomon et al. (2002 [8]) and data evaluated and used in the atrazine monograph [1]. Data and results / conclusions of the UK-report are presented in section 6.1 and Annexes 1 and 2 to this data sheet.

Data used in this data sheet are drawn from the atrazine monograph [1] and the report provided by the UK Environment Agency [5]. As regards possible effects of atrazine on endocrine regulation, these data sources were supplemented by a recent US-EPA "White Paper" dealing with this topic [9].

6.1 Chronic toxicity to aquatic organisms

In this section the data analysis and SSD-based QS-proposals of the report provided by the UK Environment Agency [5] are summarized. Underlying data and details of the SSDs set up with different data sets are collated in Annexes 1 (tables A1-A3) and 2.

Based on the data shown in tables A1-A3 of Annex 1, species sensitivity distributions (SSDs) were set up in the UK-report for several combinations of data, taking account of uncertainties:

1. The most sensitive data of all 50 species for that data are available.

2. The most sensitive data for all 21 plant species (reflecting the herbicidal mode of action of atrazine)

3. When more than one datum was available for the same endpoint and the same species a geometric mean was calculated (as recommended in the TGD) for all 50 species.

4. When more than one datum was available for the same endpoint and the same species a geometric mean was calculated (as recommended in the TGD) for the 21 plant species.

5. Only data in Table A1 for which full information on test duration and endpoint was available from the sources cited above. This had the effect of removing a suspiciously low value for the alga *Raphidocellus subcapitata*, plus removing all studies on endocrine disruption, hence leaving just standard toxicity endpoints. Again, there were two analyses for these data: one using the most

[1] Alterra Green World Research, NL-Wageningen

sensitive value when there were multiple results for the same species and endpoint, and one using the geometric mean of these values.

6. Only data that feature in the 1996 atrazine monograph produced by the UK rapporteur under Council Directive 91/414/EEC Regulation 3600/92 (Annex 1, Table 2). Again, there were two analyses for these data: one using the most sensitive value when there were multiple results for the same species and endpoint, and one using the geometric mean of these values.

7. A repeat of the analyses in 5 and 6 above using only plant species (algae and macrophytes) and removing data only reported as 'less than' values.

An original intention was also to examine 'endocrine disrupting' effects in a separate SSD. However, examination of the data showed that these studies varied widely in the types of endpoint measured, from plasma biomarkers in fish to effects on frog gonadal histology and through to more conventional reproduction endpoints in waterfleas. It therefore made little sense to analyse them in a separate SSD as the results would be meaningless. Therefore the only slightly more rational decision to include these data in the main analysis was taken, so that their position in the overall distribution could be determined. This also takes account of earlier Member State concerns that such effects should be considered in the derivation of QS for atrazine.

Finally, the mesocosm/microcosm analysis performed by van den Brink and Brock (2002) [6] was repeated using,

8. Data from studies in which only Class 1 effects (≈no effects) were reported and,

9. Geometric means of data classified as causing Class 1 (no effects) and Class 2 (slight) effects (a repeat of the van den Brink and Brock (2002) analysis) (Input data for 8. & 9 shown in Annex 1, Table 3).

The ETX software developed by Van Vlaardingen et al. (2003) [7] was used for the SSD analyses. The SSDs are shown in Annex 2.

Results are summarised in the UK-report [5] as follows:

HC5[2] values based on single species laboratory data from the fullest data set (n = 50, including some uncertain data) ranged from 0.107 to 0.492 ug/L, a factor of less than 5, generally fitted a normal distribution, and did not differ substantially when logistic or triangular distributions were used.

When only data are used for which full information is available in the Alterra database, the HC5s are 1.38 ug/L (most sensitive data) and the very similar 1.51 ug/L (geometric mean data). This contrasts with HC5 values calculated for only those data that feature in the 91/414 monograph of 2.56 ug/L (most sensitive data) and 3.06 ug/L (geometric mean data).

It could be argued that the herbicidal mode of action of atrazine means that the focus of regulatory attention should be on toxicity to algae and macrophytes. If this is the case, then HC5 values for these taxa, based upon the most reliable data, are around 1.0 to 1.5 ug/L (n=10).

However, a risk assessment based on the herbicidal mode of action of atrazine in plants clearly does not take account of an endocrine disruption mode of action in vertebrate animals. Data on the effects of atrazine on salmon olfaction and reproduction, and on amphibian gonadal histology are therefore of concern. Although the quality of both sets of data was criticised by Solomon et al. (2002) [8], other experts have not been so critical (e.g., the September 2003 meeting of the Environmental Panel of the UK Advisory Committee on Pesticides). The effects observed in these studies therefore cannot currently be dismissed as trivial or an error and, if repeated, could lead to a deterministically-based QS for atrazine of <0.004 ug/L, based on application of an AF of 10 to the

[2] HC5 = 5-percentile value of the species sensitivity distribution, i.e. the "Hazardous Concentration" (HC) at which 5% of the species in an ecosystem may suffer adverse effects. (Term also used: 5% cut-off value (5%-COV))

salmon data (see table A1). The inclusion of these 'endocrine' data in an overall analysis leads to an HC5 of 0.26 ug/L. However, such an analysis is largely meaningless as it compares incommensurable endpoints, e.g., plasma biomarkers of endocrine disruption and mortality in different species of fish and leads to overprotection of standard endpoints and underprotection of endocrine endpoints – the worst of both worlds.

In the absence of compatible data, it is considered best (in [5]) to concentrate on the SSDs that use standard endpoints alone and compare these with the results from semi-field studies as a form of 'ground-truthing' for the herbicidal effects of atrazine. Potential endocrine disrupting modes of action and effects should be considered separately.

The SSDs set up with the data from semi-field studies (table A3) resulted in a HC5 of 2.89 µg/l for Class1 (no-effect) data and a HC5 of 2.34 µg/l for the geometric mean of Class1 (no effect) and Class2 (slight transient effects) data.

6.2 Acute toxicity to aquatic organisms

The acute LC/EC50s for the most sensitive freshwater species tested identified in the risk assessment monograph [1] are: 3.96 mg as/l) for rainbow trout; 5.29 mg as/l for *Daphnia pulex*; 20.5 µg as/l for *Scenedesmus subspicatus;* 22 µg as/l for *Lemna gibba*. (Detailed data on acute toxicity of atrazine are given in annex B.8 of the monograph.)

6.3 Toxicity to marine species

Long-term toxicity data are available for marine fish, invertebrates and algae (see table A1). Acute toxicity data for various marine species are cited and evaluated in the monograph [1]. The most sensitive tested were juvenile spot (fish; 96 h LC50 8.5 mg as/l), the copepod *Acartia tonsa* (96 h LC50 4.3 mg as/l), the alga *Dunaliella tertiolecta* (120 h E_bC_{50} 0.17 mg as/l) and the diatom *Skeletonema costatum* (120 h E_bC_{50} 0.055 mg as/l). All quoted toxicity values are comparable with those of the most sensitive freshwater species. (Detailed data on the toxicity of atrazine to marine organisms are given in annex B.8 of the monograph.)

6.4 Mammalian and avian toxicity data

Data are drawn from the risk assessment monograph [1].

Table 6.1: Mammal and bird oral toxicity data relevant for the assessment of non compartment specific effects relevant for the food chain (secondary poisoning)

Type of study	**Species, test result**	**Ref.**
Long-term toxicity to mammals		
Acute dietary toxicity to birds	LD50: 940 (603-1658) mg as/kg bw	[1]
Reproductive toxicity to birds	NOEC: 225 ppm (determined for both mallard duck and bobwhite quail)	[1]

6.5 Metabolites

Data and conclusions are drawn from the risk assessment monograph [1].

Atrazine metabolites are considered significantly less toxic than atrazine itself. In terms of exposure, in surface water atrazine itself is the only environmentally significant residue where contamination results from spray drift [1].

The risk to aquatic organisms has been addressed through a number of microcosm and mesocosm studies. These studies involved realistic degradation processes, hence the organisms therein would have been exposed to realistic levels of metabolites of atrazine. There is no reason to suggest that hydroxyatrazine or desethylatrazine would have a high toxicity to fish or aquatic invertebrates considering the previously submitted data for both the parent compound and a range of other metabolites. Further reassurance for hydroxyatrazine specifically is provided by a newly submitted study on the herbicidal activity of this metabolite. This study showed this metabolite to have little or no activity compared with the parent compound, suggesting that the metabolite will be significantly less toxic to either aquatic plants or green algae than the parent compound

6.6 Summary on endocrine disrupting potential

In the Communication from the Commission to the Council and the European Parliament on the implementation of the Community Strategy for Endocrine Disrupters, atrazine is classified as a substance with evidence of endocrine disruption or evidence of potential ED [2] .

In the risk assessment monograph [1] a study in Fischer-344 rats is reported. It is stated that exaggerated dosage and duration provided results suggestive that atrazine may produce an endocrinological disturbance leading to an exacerbation of tumorigenicity in endocrine-responsive tissues in the rat. The study however is considered flawed by lack of detail in the paper, and by increased survival in the high dose animals which may have skewed the tumour incidence. Possible adverse effects of atrazine on endocrine regulation in aquatic organisms are not addressed in the monograph.

The US-EPA, in a “White Paper” issued in 2003 [9], concludes that the weight-of-evidence based on currently available studies does not show that atrazine produces consistent, reproducible effects across the range of exposure concentrations and amphibian species tested. The current body of knowledge is considered to have deficiencies and uncertainties that limit its usefulness in interpreting potential atrazine effects. Specifically, the demasculinizing (decreased laryngeal dilator muscle area) effects were not replicated in multiple laboratories [9]. Additionally, the feminizing effects (intersex/hermaphroditism/ovotestes) of atrazine were observed in three laboratory studies whose experimental designs could not be easily reconciled and that reported significant effects at different concentrations: one at 25 ug/L atrazine and the other two at 0.1 ug/L. While the feminizing effects observed in these different studies were consistent qualitatively, there was no consistency across the studies in the reported dose-response relationships. That inconsistency, together with the limitations in methodology in each study, does not allow a reliable determination of causality or the nature of any dose-response relationship. Although the Florida cane toads monitored in the field exhibited both demasculinizing effects (genetic males with female coloration) and feminizing effects (oogenesis in male Bidder’s organ), there were insufficient data to conclusively link atrazine exposure to the phenomena. Thus, the available data do not establish a concordance of information to indicate that atrazine will or will not cause adverse developmental effects in amphibians. [9]

7 Effect data (human health) [1]

Data and conclusions are drawn from the risk assessment monograph [1].

Table 7.1: Summary human toxicology data [1]

	Value	Study	Safety factor
ADI	0.005 mg/kg/day	NOAEL of 0.5 mg/kg/day from the critical carcinogenicity study in Sprague-Dawley rats	100

Long term toxicity and carcinogenicity	Atrazine was not carcinogenic in an adequate study in a second strain of rat (Fischer 344). However, a second study in the Fischer-344 using exaggerated dosage and duration provided results suggestive that atrazine may produce an endocrinological disturbance leading to an exacerbation of tumourigenicity in endocrine-responsive tissues in the rat. Mammary carcinogenesis appears to occur only under specific conditions.... The tumourigenicity is therefore considered a consequence of endocrine disturbance and to be irrelevant to humans at doses where no endocrine disturbance occurs. Regulating exposure on the basis of the no-effect level is therefore appropriate. Classification of atrazine as a carcinogen is not appropriate.
Genotoxicity	In view of a considerable weight of negative data generated by appropriate studies, atrazine is concluded to be non-genotoxic.
Mutagenicity	In the genotoxicity results presented for review, atrazine was shown not to be mutagenic.
Reproductive toxicity	Atrazine caused no teratogenicity at any dose level, irrespective of maternal toxicity, in adequate studies in 2 species. The no-effect level for maternal and embryofoetal effects was 2.5 mg/kg/day, derived from the multigeneration study where effects were found at 500 ppm (ca. 25 mg/kg/day). 5 mg/kg/day may be a low-effect level for minor and reversible delayed ossifications.

8 Calculation of quality standards

Supported by opinions expressed by Member State experts or published in the literature, it is deemed that at present not enough reliable information is available to set a quality standard based on the potential endocrine effects of atrazine (see sections 6.6 and 6.1). Therefore, the suggested QS do not cover potential effects of this substance on the endocrine system but are based on “classical” toxicological endpoints such as mortality, development, reproduction etc. If in the future data become available that provide firmer evidence that endocrine effects of atrazine might be a relevant concern it will be necessary to revise the proposed QS.

In the case of atrazine enough data are available to employ statistical extrapolation as supplementary approach to the standard assessment factor method in order to derive quality standard proposals for the protection of the pelagic community.

Due to the specific mode of action demonstrated for atrazine, difference of sensitivity between freshwater and marine species is not expected. This expectation is supported by comparison of toxicity test data for freshwater and marine fish, crustacea and algae evaluated in the risk assessment monograph or cited in the consolidated data base of the UK-report for atrazine and other data listed in table A1 – A2. All these data indicate that the sensitivity of marine species is comparable to that of freshwater species of the same taxonomic group. In accordance with guidance provided in the revised TGD it is therefore suggested to use the quality standard derived

for the protection of the pelagic community of inland waters as well for all other surface waters covered by the Water Framework Directive.

Atrazine metabolites are significantly less toxic than atrazine itself [1] (see section 6.5 of this data sheet). It is therefore not necessary to consider these metabolites for the purpose of quality standard setting.

8.1.1 Quality standards for water derived by the assessment factor method

Annual average quality standard (AA-QS)

Algae and higher plants are the most sensitive among the species for that toxicity tests are available (fish, amphibia, crustaceans, insects, rotatoria, cyanobacteria, algae, higher plants; see tables A1 and A2). The lowest NOEC reported in the monograph [1] is the *Lemna gibba* NOEC of <3.4 µg/l (table A2). However, in the UK-report [5] (tab. A1) even lower NOECs in the range of 0.016 – 3 µg/l are reported for the algae *Raphidocellus subcapitata* (0.016 µg/l), *Laminaria hyperborea* (1 µg/l), *Scenedesmus subspicatus* (2 µg/l), *Scenedesmus acutus* (3 µg/l) and the cyanobacteria *Anabaena flos-aquae* (0.1 µg/l) and *Microcystis aeruginosa* (1.5 & 3 µg/l). Although doubts are raised with regard to the validity of the *Raphidocellus* NOEC in the UK-report (see Annex 2) and for some of the tests the effects observed or the test duration are not reported (rendering those tests invalid according to the agreed quality criteria [4]), the results suggest a NOEC of atrazine in the range of 1 – 3 µg/l.

Because long-term data are available for more than the minimum of 3 different taxonomic groups, the NOEC is divided by an assessment factor of 10 in order to derive the long term quality standard for surface water.

QS_{water} = NOEC (1-3 µg/l) / AF (10) = 0.1 – 0.3 µg atrazine / l

The log Kp_{susp} is only 0.93 and the water solubility is high. Thus the trigger criterion to calculate a corresponding $QS_{SPM.water}$ referring to the concentration of atrazine in suspended particulate matter (SPM) is not met (see table 8.1 of [4]).

Quality standard accounting for transient concentration peaks (MAC-QS)

Acute toxicity data are available in the monograph [1] for a range of freshwater and saltwater organisms (fish, crustaceans, insects, cyanobacteria, algae and higher plants). The lowest EC50 value is 20.5 µg as/l obtained with the alga species *Scenedesmus subspicatus* (see section 6.2 of this data sheet).

The MAC-QS is derived on the basis of this EC50 and the guidance given in the TGD on the effects assessment for intermittent releases (section 3.3.2 of part II of [3]). As atrazine is a herbicide with a specific mode of action and the most sensitive organism is a plant, it is suggested to use only a reduced assessment factor of 10 (instead of 100).

MAC-QS = 20.5 µg/l / AF (10) = 2 µg Atrazine / l

This value is in agreement with the lowest concentrations at that no effects or slight transient effects (i.e. with no longer-term ecological relevance) have been observed in mesocosm studies (2 – 5 µg/l, see table A3).

8.1.2 Quality standards for water derived by statistical extrapolation

Annual average quality standard (AA-QS)

In the UK-report [5] a range of different selections of data were analysed by means of statistical extrapolation, i.e. calculating the 5-percentile of the data set assuming log-normal distribution (see section 6.1 and Annex 2). Among the data selections explored were different sets of single-species NOEC data and two sets of semi-field data (i.e. (no-)effect data observed in mesocosms).

As plants are the most sensitive organisms (atrazine is a herbicide with a specific mode of action on the photosynthetic system), it could be considered to base the AA-QS on a SSD set up with algae and higher plant long-term toxicity data. Respective calculations in the UK-report with data meeting the quality requirements (full report of study parameters such as study duration, effects observed, endpoint etc.) resulted in 5-percentile cut-off values (≈HC5) of 1.05 µg/l if the most sensitive NOEC per species were used and 1.51 µg/l if the geometric means of the species NOECs served as input data. In the latter case however, the input data failed to meet the goodness of fit test (see Annex A2, figures 6 and 8).

There are however as well data from semi-field tests (mesocosms) available. Data obtained with such test systems are usually considered to have the highest relevance for field situations because they are designed to meet the structure of natural communities and water quality parameters of natural aquatic systems as close as possible. Hence effects of a toxicant on communities and its fate in the system can be studied in such systems.

It is therefore suggested to derive the AA-QS for the protection of the pelagic community by using mesocosm data. These data are available from several studies, covering several types of effects (see table A3 of Annex 1). As the TGD stipulates to use only long-term no-effect data for statistical extrapolation of the PNEC, it is suggested to rely on available mesocosm NOECs for the derivation of the AA-QS ("class 1" data in table A3). The TGD does not include a recommendation to use the 5-percentile of a distribution set up with mesocosm data to derive a threshold value for risk assessment (e.g. a PNEC). However, there do no scientific reasons exist as to why mesocosm NOECs could not be used the same way as single species tests NOECS in establishing such a distribution and threshold value. Therefore, this approach has been used in the report of the UK Environment Agency as well (see Annex 2).

Using the ETX-software [7] (which is based on the statistical extrapolation method for calculating the 5-percentile of a log-normal distribution by Aldendberg and Jaworska [10]), it could be shown in the UK-study that the data set is normally distributed (Anderson Darling goodness of fit = 0.593, $p<0.1$). The resulting sensitivity distribution for these mesocosm NOECs (n=6) is shown in figure 1. The 5%-cut-off value (5%-COV ≈ HC5) is 2.893 ug/L, with a lower 95%-confidence limit of 0.879 ug/L and an upper confidence limit of 4.93 ug/L. [5]

For the derivation of the final PNEC (≈ quality standard) the TGD recommends to apply an additional assessment factor in the range of 5 – 1 on the 5%-COV, accounting for further uncertainties. With regard to the Higher-Tier mesocosm data available for atrazine these uncertainties are:

1. *Statistical uncertainties around the 5th percentile:* 2 SSDs using microcosm/mesocosm data are reported in the UK-report [5]. One SSD was set up using only NOEC data (see figure 1 of this data sheet). The resulting 5%-COV is 2.9 µg/l. The second SSD was calculated with geometric means of Class 1 and Class 2 data (Class 2 ≈ "slight effects"), resulting in a lower HC5 of 2.3 µg/l. This example highlights the dependence of the resulting 5%-COV on the accidental composition of the input data set (Class 2 effects in some studies are lower than class 1 effects reported in other studies). Further, in the microcosm/mesocosm data set (see table A3) there

are “clear effects” (Class 4) in 3 other studies at concentrations of 10-15 µg/l reported, i.e. in the same range than the “no effects” observations (5-20 µg/l) in the studies used to establish the SSDs. Calculation of a SSD with the Class 4 data reported in table A3 results in a 5%-COV of 6 µg/l, i.e. only 2 times higher than the result for the Class 1 “no effects” data (this low ratio indicates a small margin between the occurrence of “no effects” and “clear effects” and justifies the application of a rather high assessment factor).

2. *Microcosm/mesocosm study design:* Some of the (no)effect levels reported in table A3 appear to refer to the initial nominal concentrations. However, only (no)-effect levels expressed as time-weighted average concentrations should be the basis for QS derivation[3]. This requirement may not be of particular relevance for atrazine, as the substance has a long DT50 in water (28-134 d), but it might partition to sediment (20-30% within 7-28 days, as stated in the monograph). Hence, the time-weighted average concentration in the test systems way have been lower than reported.

3. *Representativeness of the test systems for the water bodies to be covered by the QS:* The QS must be protective for all types of surface waters and communities that are addressed by the respective standard, as long as it is not possible to rule out that exposure to plant protection products may occur in particular types of water bodies. This means that in the interpretation of Higher-Tier studies an evaluation is necessary as to whether the test system and the tested community, respectively, can be considered representative for all water bodies that potentially are subject to plant protection product exposure. Higher-Tier studies in the context of the plant protection product risk assessment are usually focused to euthrophic water bodies occurring in the immediate vicinity of agriculturally used areas. A QS under the WFD, however, must assure protection also for water bodies that significantly differ from this paradigm.

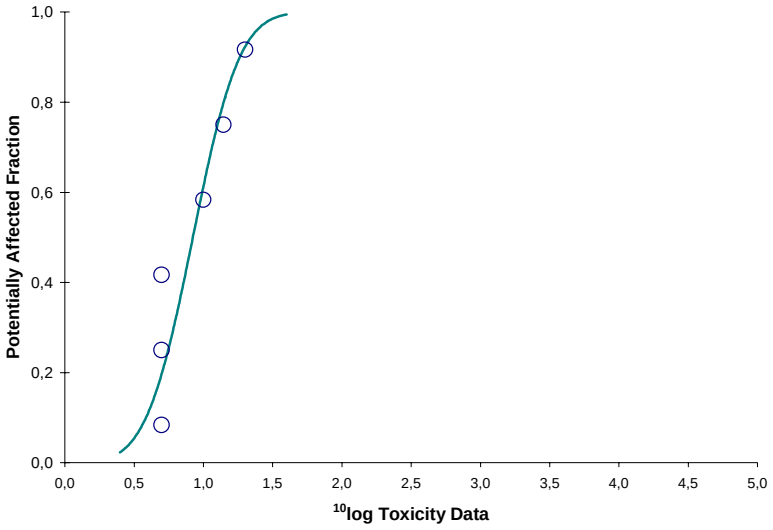

Figure 1: SSD for Class 1 (≈NOEC) data from mesocosms dosed with atrazine [5] (input data see table A3)

[3] Differences in the objectives of the risk assessment for plant protection products and environmental quality standard setting are described in the Manual (section 4.3.5) [4].

Taking account of the uncertainties addressed in points 1 – 3 above, an **assessment factor of 5** is suggested to derive the QS.

QS_{water} = 5%-COV (2.9 µg/l) / AF 5 = 0.6 µg atrazine /l

Because the AA-QS obtained by statistical extrapolation is based on the results of several mesocosm studies with a more realistic and environmentally relevant test design than single species tests, it is suggested to prefer the value obtained by this method over the figure obtained with the classical assessment factor approach based on the most sensitive single species NOEC.

The log Kp_{susp} is only 0.93 and the water solubility is high. Thus the trigger criterion to calculate a corresponding $QS_{SPM.water}$ referring to the concentration of atrazine in suspended particulate matter (SPM) is not met (see table 1a of [4]).

The suggested QS does not cover potential effects of this substance on the endocrine system although endocrine effects of atrazine may be a relevant concern. However, supported by opinions expressed by Member State experts or published in the literature it is deemed that at present not enough reliable information is available to set a quality standard based on the potential endocrine effects of atrazine.

8.2 Quality standard for sediment

The log Kp_{susp} is only 0.93 and the water solubility is high. Thus the trigger criterion to calculate a $QS_{sediment}$ are normally not met (see table 1a of [4]). However, it is stated in the risk assessment monograph [1] that 20-30% of applied atrazine will partition into the sediment after 7-28 days and, therefore, atrazine entering surface waters may pose a risk to sediment dwelling invertebrates.

Hence, it is deemed useful to derive an indicative value for sediment.

No data are available for sediment toxicity tests. According to the Manual (sections 4.3.2.3 & 4.3.2.4) [3], the $PNEC_{sediment}$ ($\approx QS_{sediment}$) may be calculated using the equilibrium partitioning method in the absence of ecotoxicological data for sediment-dwelling organisms.

The equilibrium partitioning approach only considers uptake via the water phase. However, uptake may also occur via other exposure pathways like ingestion of sediment and direct contact with sediment. There is evidence from studies in soil that the proportion of the total dose remains low for chemicals with a log Kow up to 5. As the log Kow of atrazine is only 2.5 exposure routes other than direct uptake via the water phase need not to be considered and the $QS_{sediment}$ is calculated as follows:

$$QS_{sed.wet\_weight}\ [mg.kg^{-1}] = \frac{Kp_{SPM\text{-}water}\ [2.15\ m^3/m^3]}{bulk\ density_{SPM.wet}\ [1{,}150\ kg/m^3]} * 1{,}000 * QS_{water}\ [mg/l]$$

with:

$K_{SPM\text{-}water}$ = f_{solid} (0.1) * Kp_{susp} (Koc (86) * foc (0.1) [l/kg]) / 1000 * RHO_{solid} (2500 kg/m^3) = 2.15 m^3/m^3 (sect 2.3.5 of [3])

bulk $density_{SPM.wet}$ = 1150 kg/m^3

1000 = conversion factor m^3/kg to l/kg

QS_{water} = 0.0006 mg/l

The TGD defines wet SPM as 90% vol/vol water (density 1 kg/l) and 10% vol/vol solids (density 2.5 kg/l), thus giving a wet density of (0.9 × 1) + (0.1 × 2.5) = 1.15 kg/l. The dry weight of solids is therefore 0.25 kg (per litre wet SPM) and thus the wet:dry ratio is 1.15/0.25 = 4.6.

This results in the following quality standards for sediment (wet and dry weight):

$QS_{sediment}$	1.12 µg/kg (wet wt)	5.2 µg/kg (dry wt)

The values derived by the EP-method should only be considered as tentative standards. In order to refine the quality standards for the sediment compartment long term tests conducted with benthic organisms are required. For the time being no reliable $QS_{sediment}$ can be derived.

8.3 Secondary poisoning of top predators

Since the BCF_{fish} (whole body) is only 12 and the log Kow is only 2.5 the calculation of a quality standard referring to the protection of top predators from secondary poisoning is not required (trigger value not met).

8.4 Quality standards referring to food uptake by humans

Atrazine is not classified as having CMR-properties and it has only a very low bioaccumulation potential ($BCF_{fish} \approx 12$). Therefore the triggers values are not met that require the derivation of a quality standard referring to the prevention of adverse effects on human health due to the ingestion of food from aquatic environments.

8.5 Quality standards for drinking water abstraction

The imperative A1 value referring to drinking water abstraction by simple treatment is 1 µg/l for the total amount of pesticides (Council Directive 75/440/EEC). The drinking water standard (DWS) set in CD 98/83/EC is 0.1 µg/l for individual pesticides.

The DWS is a limit value never to be exceeded at the tap. The MAC-QS (ECO) derived for the protection of the freshwater community (2.9 µg/l) may therefore not suffice to allow for compliance with the DWS if only simple purification techniques (category A1 of CD 75/440/EEC, i.e. filtration and disinfection) are used for the abstraction of drinking water from surface water bodies according to Art. 7 of the WFD.

An assessment by experts in drinking water technology with regard to the question which fraction of the amount of atrazine present in raw water can be removed by usual simple treatment procedures might be helpful. If the respective fraction were known, this figure could be used together with the drinking water standard to set the maximum acceptable concentration in surface water bodies designated for the **a**bstraction of **w**ater **i**ntended for **h**uman **c**onsumption (AWIHC).

MAC-QS (AWIHC) = DWS (0.1 µg/l) / fraction not removable by simple treatment

8.6 Overall quality standard

0.6 µg atrazine /l may apply as overall annual-average quality standard (AA-QS) and 2 µg/l as MAC-QS for all types of surface waters covered by the Water Framework Directive. If the drinking water standard is exceeded in areas designated for the abstraction of water intended for human consumption in accordance with Art. 7 of the WFD, specific measures need to be taken in order to guarantee compliance with the drinking water standard at the tap.

9. References

[1] UK Rapporteur Monograph, Council Directive 91/414/EEC: Atrazine, Volume 1 (Report and Proposed Decision of the United Kingdom made to the European Commission under Article 7(1) of Regulation 3600/92), Levels 1-4 without Annexes; OCTOBER 1996. In Addition: Volume 3, Annex B (ADDENDUM to the Report and Proposed Decision of the United Kingdom made to the European Commission under Article 7(1) of Regulation 3600/92) Summary, Scientific Evaluation and Assessment, February 2000

[2] COM(2001)262 final: Communication from the Commission to the Council and the European Parliament on the implementation of the Community Strategy for Endocrine Disrupters – a range of substances suspected of interfering with the hormone system of humans and wildlife.

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[12] ESIS: European Chemicals Bureau – ESIS (European Substances Information System), January 2005. http://ecb.jrc.it/existing-chemicals/ ⇒ tick ESIS button, then enter CAS or EINECS number of substance.

Annex 1: Consolidated data base – atrazine aquatic toxicity [5]

Table A1: Atrazine single species data [5]. References with a prefix 'n' refer to data on the Alterra database and 'cd Syngenta' refers to data supplied to Alterra by Syngenta. (Concentration = NOEC or equivalent)

Taxon	Species Latin Name	Effect	Duration (days)	Concentration (ug/l)	> or <?	Reference
Vertebrate	*Alligator mississippiensis*	Hatchability, mortality & gonad histology		500.00	>	Gross et al. (1999a)
Vertebrate	*Ambystoma tigrinum*	Time to metamorphose		75.00	<	Larson et al. (1998)
Vertebrate	*Brachydanio rerio*	Mortality	35	300		n4244
Vertebrate	*Carasius auratus*	Female 11-ketotestosterone concentration		100	<	Spano et al. (2002)
Vertebrate	*Cyprinodon variegatus*	Mortality	31	1900		n4803
Vertebrate	*Cyprinus carpio*	Mortality	8	670		Von Pluta (19xx)
Vertebrate	*Ictalurus punctatus*	Mortality	9	13		Birge et al. (1979)
Vertebrate	*Lepomis macrochirus*	-	90	95		n6067
Vertebrate	*Micropterus salmoides*	Male 11-ketotestosterone concentration		35		Wiesner & Gross (2001)
Vertebrate	*Oncorhynchus mykiss*	Development	60	5.7		Von Pluta (19xx)
Vertebrate	*Pimephales promelas*	-	60	210		n7323
Vertebrate	*Pimephales promelas*	-	274	250		n7324
Vertebrate	*Pimephales promelas*	Reproduction	274	150		CD Syngenta (1510)
Vertebrate	*Rana pipiens*	Mortality	56	310		n6589
Vertebrate	*Rana sylvatica*	Hatchability & post-hatch mortality		20000	>	Allran & Karasov (2001)
Vertebrate	*Salmo salar*	Expressible milt		0.04	<	Moore & Waring (1998)
Vertebrate	*Salvelinus fontinalis*	-	308	65		n7378
Vertebrate	*Trachemys elegans*	Hatchability, mortality & gonad histology		500	>	Gross et al. (1999b)
Vertebrate	*Xenopus laevis*	Gonadal abnormalities		0.1	<	Hayes et al. (2002)
Invertebrate	*Brachionus calyciflorus*	Full lifecycle	10	5000		Girling et al. (2000)
Invertebrate	*Ceriodaphnia dubia*	Reproduction	7	2500		n4392
Invertebrate	*Ceriodaphnia dubia*	Reproduction	7	1200		EU/ECCO (1996)
Invertebrate	*Ceriodaphnia dubia*	Reproduction	7	1200		cd Syngenta (1375)
Invertebrate	*Chironomus riparius*	Mortality	70	110		Macek et al. (1976)
Invertebrate	*Chironomus tentans*	Mortality	70	110		n4528

Taxon	Species Latin Name	Effect	Duration (days)	Concentration (ug/l)	> or <?	Reference
Invertebrate	*Daphnia pulicaria*	Production of males		5		Dodson et al. (1999)
Invertebrate	*Daphnia magna*	Reproduction	64	140		Macek et al. (1976)
Invertebrate	*Daphnia magna*	-	21	140		n4402
Invertebrate	*Daphnia magna*	Reproduction	21	40		EU/ECCO (1996)
Invertebrate	*Daphnia magna*	Reproduction	28	1000		Schober & Lampert (1977)
Invertebrate	*Daphnia magna*	FCD	21	40		cd Syngenta (73)
Invertebrate	*Daphnia magna*	TCNY	21	120		cd Syngenta (73)
Invertebrate	*Daphnia pulex*	Growth	28	1000		n4911
Invertebrate	*Daphnia pulex*	Growth	28	2000		n4912
Invertebrate	*Eurytemora affinis*	Mortality	8	4200		14910
Invertebrate	*Eurytemora affinis*	Mortality	8	17500		Hall et al (1995)
Invertebrate	*Eurytemora affinis*	Mortality	8	12250		Hall et al (1995)
Invertebrate	*Gammarus fasciatus*	Reproduction	119	60		n5214
Invertebrate	*Gammarus lacustris*	-	30	60		n5294
Invertebrate	*Gammarus pulex*	Precopula separation	not recorded	100		Girling et al. (2000)
Invertebrate	*Americamysis bahia*	Mortality	life cycle	80		Ward & Ballantine (1985)
Alga	*Anabaena flos-aqua*	-	5	0.1		n4023
Alga	*Chlamydomonas geitleri*	Growth	not recorded	110		Francois & Robinson (1990)
Alga	*Chlamydomonas reinhardtii*	Growth	10	3.7		Schafer et al.(1994)
Alga	*Chlorella pyrenoidosa*	Growth	3	16		n4557
Alga	*Chlorella saccharophila*	.	4	5		Carrasco et al. (1997)
Alga	*Dunaliella tertiolecta*	-	5	100		n5074
Alga	*Dunaliella tertiolecta*	Cell counts	5	100	<	cd Syngenta (75)
Alga	*Euglena gracilis*	Growth	5	6300		Girling et al. (2000)
Alga	*Euglena gracilis*	Growth	5	39000		Girling et al. (2000)
Alga	*Laminaria hyperborea*	Growth	2	1		n5523
Alga	*Microcystis aeruginosa*		not recorded	1.5		n5885

Taxon	Species Latin Name	Effect	Duration (days)	Concentration (ug/l)	> or <?	Reference
Alga	*Microcystis aeruginosa*	Growth	8	3		n5886
Alga	*Navicula pelliculosa*	-	5	10		n6821
Alga	*Navicula pelliculosa*	Cell counts	5	100	<	cd Syngenta (75)
Alga	*Nitzschia sigma*	Photosynthesis	7	22		n6075
Alga	*Nitzschia sigma*	Growth	7	220		n6087
Alga	*Scenedesmus acutus*		4	3		Carrasco et al. (1997)
Alga	*Scenedesmus costatum*	-	5	14		n7392
Alga	*Scenedesmus quadricauda*		not recorded	15		n6648
Alga	*Scenedesmus quadricauda*	Growth	8	30		n6651
Alga	*Scenedesmus subspicatus*	Growth	4	22		4008
Alga	*Scenedesmus subspicatus*	Growth	1	2		Girling et al. (2000)
Alga	*Scenedesmus subspicatus*	Growth	3	22		Girling et al. (2000)
Alga	*Scenedesmus subspicatus*	Growth	2	20		Schafer et al.(1994)
Alga	*Scenedesmus subspicatus*	Growth	4	40		n6655
Alga	*Scenedesmus subspicatus*	Growth	3	10		EU/ECCO (1996)
Alga	*Scenedesmus subspicatus*	Growth	3	32		cd Syngenta (1820)
Alga	*Scenedesmus subspicatus*	Growth	3	9.6		cd Syngenta (1820)
Alga	*Scenedesmus subspicatus*	Growth	3	21		cd Syngenta (1869)
Alga	*Scenedesmus subspicatus*	Growth	3	11		cd Syngenta (76)
Alga	*Scenedesmus subspicatus*	Growth	3	3.7		cd Syngenta (10)
Alga	*Raphidocellus subcapitata*	-	5	0.016		n7396
Alga	*Raphidocellus subcapitata*	Growth	3	70		n6686
Alga	*Raphidocellus subcapitata*	Biomass	4	75		18093
Alga	*Raphidocellus subcapitata*	-	5	76		n7408
Alga	*Raphidocellus subcapitata*	Growth	5	16		EU/ECCO (1996)
Alga	*Raphidocellus subcapitata*	Growth	4	18		EU/ECCO (1996)
Alga	*Raphidocellus subcapitata*	RCD	4	76		cd Syngenta (1371)
Alga	*Raphidocellus subcapitata*	Cell counts	5	16		cd Syngenta (1721)
Alga	*Skeletonema costatum*	Growth	5	14		EU/ECCO (1996)

Taxon	Species Latin Name	Effect	Duration (days)	Concentration (ug/l)	> or <?	Reference
Alga	*Skeletonema costatum*	Growth	5	14		cd Syngenta (1722)
Alga	*Thalassiosira fluviatilis*	Growth	7	22		n6768
Macrophyte	*Lemna gibba*	-	14	7.7		n5793
Macrophyte	*Lemna gibba*	-	14	10		n5798
Macrophyte	*Lemna gibba*	Frond production	14	8.3		EU/ECCO (1996)
Macrophyte	*Lemna gibba*	Biomass	14	8.3		EU/ECCO (1996)
Macrophyte	*Lemna gibba*	Frond production	14	8.3		cd Syngenta (1868)
Macrophyte	*Potamogeton pectinatus*	Weight	28	15		Hall & Anderson (1997)
Macrophyte	*Typha latifolia*	Growth	7	100		Moore et al. (1999)

Table A2: Atrazine data taken from 91/414 monograph (1996) and used in reference [5]. (Concentration = NOEC or equivalent)

Taxon	**Species Latin Name**	**Effect**	**Duration (days)**	**Concentration (ug/L)**	**> or <?**
Vertebrate	*Oncorhynchus mykiss*	Mortality & behaviour	21	60	
Vertebrate	*Pimephales promelas*	Full life-cycle	274	250	
Invertebrate	*Ceriodaphnia dubia*	Reproduction	7	1200	
Invertebrate	*Daphnia magna*	Reproduction	21	40	
Alga	*Dunaliella tertiolecta*	Cell counts	5	100	<
Alga	*Navicula pelliculosa*	Cell counts	5	100	<
Alga	*Scenedesmus subspicatus*	Growth	3	10	
Alga	*Selenastrum capricornutum*	Growth	5	16	
Alga	*Selenastrum capricornutum*	Growth	4	18	
Alga	*Skeletonema costatum*	Growth	5	14	
Macrophyte	*Lemna gibba*	Frond production & biomass	14	8.3	
Macrophyte	*Lemna gibba*	Frond production	14	3.4	<

Table A3: Classification of the most sensitive endpoints in laboratory and field model experiments that study the ecological impact of exposure to atrazine (source: [6]). Exposure concentrations are expressed in µg/l (nominal). The observed effects are classified according to magnitude and duration.

The study no. 1h was excluded form analysis because of its deviating exposure pattern (short-tem pulse)

Class 1: No effects demonstrated
Class 2: Slight effects: Confined responses of sensitive endpoints. Effects observed on individual sampling occasions only and/or of a short duration directly after treatment
Class 3: Clear short-term effects. Convincing reductions in sensitive endpoints but recovery takes place within 8 weeks post treatment.
Class 4: Clear effects, recovery not studied (because duration of study was too short)
Class 5: Clear long-term effects lasting > 8 weeks

Study no (Table 5)	Exposure regime	Class 1	Class 2	Class 3	Class 4	Class 5	Type of test system
1h	Pulse (24 h)	100 µg/L	-	-	-	-	Experimental streams
1f	Single application	-	5 µg/L [A]	-	-	-	Recirculating lab streams
1g	Single application	-	-	100 µg/L [B]	1000 µg/L [C]	-	Recirculating lab streams
1l	Constant	-	-	-	10 µg/L [C]	-	Recirculating lab streams
1q	Constant	-	-	-	14 µg/L [C]	-	Flow-through exp. streams
1p	Constant	14 µg/L	25 µg/L [D]	-	80 µg/L [E]	-	Flow-through lab streams
1m	Constant	-	-	-	24 µg/L [F]	-	Recirculating lab streams
1e	Single application	-	2 µg/L [G]	-	30 µg/L [G]	-	mesocosms
1b	Single application	-	10 µg/L [H]	-	100 µg/L [H]	-	laboratory microcosms
1a	Single application	5 µg/L	50 µg/L [H]	-	100 µg/L [H]	-	laboratory microcosms
1c	Single application	20 µg/L	-	60 µg/L [H]	100 µg/L [J]	200 µg/L [J]	laboratory microcosms
1d	Single application	-	-	-	-	50 µg/L [K]	experimental ponds
1k	Repeated / constant	5 µg/L	-	-	-	-	laboratory microcosms
1j	Repeated / constant	5 µg/L	10 µg/L [H]	-	-	75 µg/L [L]	field enclosures
1n	Repeated / constant	10 µg/L	-	-	32 µg/L [H]	-	laboratory microcosms
1o	Repeated / constant	-	-	-	15 µg/L [J]	-	experimental swamps
1i	Repeated / constant	-	-	-	-	20 µg/L [M]	experimental ponds

[A] Increase insect emergence;
[B] Decrease pH and net primary production ;
[C] Decrease community metabolism and periphyton biomass
[D] Bacterial activity ;
[E] Decrease diversity periphytic algae and periphyton Chl-a;
[F] Decrease biomass periphyton
[G] Community structure algae;
[H] Community metabolism (DO, pH);
[J] Community metabolism and algae;
[K] Community metabolism, algae and macrophytes
[L] Community metabolism, primary producers and invertebrates;
[M] Community metabolism, primary producers, invertebrates and vertebrates