POSITION PAPER ON PBT PROPERTIES OF ANTIMONY

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Scope

This position paper covers the Persistence, Bioaccumulative, Toxicity (PBT) assessment of inorganic Sb-ions released from the dissolution/transformation of Sb metal or Sb compounds. The behaviour of the Sb-ion species in the environment is independent of the form of antimony compounds or minerals from which they are derived.

The REACH Regulation ((EC) 1907/2006) states that a PBT and vPvB (very persistent very bioaccumulative) assessment shall be conducted as foreseen in Article 14 (3) (d) in conjunction with Annex I Section 4 according to the criteria as laid down in Annex XIII (as updated in Commission Regulation (EU) No 253/2011 of 15 March 2011). The PBT and vPvB criteria of Annex XIII however only apply to organic substances, including organometals. Therefore, strictly spoken, there is no legal obligation for a PBT and vPvB assessment for inorganic substances.

The draft Guidance to Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of substances and mixtures for metals and metal compounds qualitatively distinguishes metals from organometals based on their dissociation behaviour upon dissolution in water: *"Organometals do not dissociate or dissolve in water as the metal ion, as metals and inorganic metal compounds do. … Metal compounds that contain an organic component but that dissociate easily in water or dissolve as the metal ion should be treated in the same way as (inorganic) metal compounds".*

The following Sb compounds from the i2a substance list beyond doubt represent inorganic substances: Sb metal, Sb_2O_3, Sb_2S_3, $SbCl_3$, Sb_2O_5, $NaSbO_3$, $SbCl_5$ and $NaSb(OH)_6$. Whereas antimony triacetate ($Sb(CH_3COO)_3$) and diantimony tris ethylene glycolate ($Sb_2(C_2H_4O_2)_3$) contain organic moieties, they also clearly constitute inorganic substances, since they lack a covalent bond between the metal and any carbon atom of the anionic organic moiety. Thus, they do not comply with the IUPAC definition of organometallic compounds, despite that results from the transformation/dissolution tests conducted for both compounds indicated that both ligands appeared to stabilise Sb(III) in solution compared to other Sb(III) substances, which showed a more pronounced oxidation of Sb(III) to Sb(V) upon dissolution (CanMET, 2010). This is, however, no direct proof for the occurrence of Sb-complexes in solution and up to 31% of the dissolved Sb is still oxidised to Sb(V) within 28 days at pH 8.5. All these inorganic Sb substances are covered by the PBT assessment of the Sb-ion released upon dissolution.

PBT criteria

The assessment approach for Persistent, Bioaccumulative, and Toxic (PBT) substances (Table 1) was established because of the possibility that some man-made chemicals may accumulate in parts of the environment, and whereby such an accumulation may cause unpredictable effects in the long term that may be very difficult to reverse.

Table 1: PBT and vPvB criteria under REACH Annex XIII (based on Regulation (EU) No 253/2011).

Property	PBT-criteria	vPvB-criteria
Persistence	• $T_{1/2}$ >60 days in marine water, or • $T_{1/2}$ >40 days in fresh- or estuarine water, or • $T_{1/2}$ >180 days in marine sediment, or • $T_{1/2}$ >120 days in fresh- or estuarine sediment, or • $T_{1/2}$ >120 days in soil.	• $T_{1/2}$ >60 days in marine, fresh- or estuarine water, or • $T_{1/2}$ >180 days in marine, fresh- or estuarine sediment, or • $T_{1/2}$ >180 days in soil.
Bioaccumulation	BCF >2,000 l/kg in aquatic species (data from freshwater as well as marine water species can be used)	BCF >5,000 l/kg

Toxicity	• long-term NOEC or EC10 <0.01 mg/l for marine or freshwater organisms, or • substance is classified as carcinogenic (category 1A or 1B), mutagenic (category 1A or 1B), or toxic for reproduction (category 1A, 1B or 2), or • there is other evidence of chronic toxicity, as identified by the classifications: STOT RE category 1 or 2) according to Regulation EC No 1272/2008.

These PBT criteria are not directly applicable to metals as it neglects various processes affecting the fate, bioavailability and toxicity of inorganic compounds. (partitioning, speciation, complexation, competition with other ions, adsorption, precipitation, dissolution etc.). The unit world model (UWM) was proposed as an alternative to the PBT criteria and has the potential to be used for the hazard assessment of both metal ions and organic chemicals. The primary advantage of the UWM approach for hazard assessment is that it goes beyond the individual consideration of persistence, bioaccumulation, and inherent toxicity by integrating them to give an overall expression of hazard in the form of a critical loading. In doing so, it circumvents the problem of the inherently infinite persistence of metals and, potentially, provides a consistent and more level playing field for assessing these diverse substances (Harvey et al., 2007). The UWM can also take into account the effect of speciation and water properties (pH, hardness etc.) on bioavailability and toxicity. However, for Sb no such models (e.g. BLM) are available and only generic partitioning, BCF (bioconcentration factor) and toxicity values are available.

Persistence

Antimony is a natural element, with an average natural abundance in the earth's crust and seawater of approximately 0.2 mg Sb/kg and 0.24 µg Sb/L, respectively (Lide, 2009). The natural background concentrations of antimony in European surface waters, soils and stream sediments with minimal anthropogenic pressure have been assessed within the FOREGS project (http://www.gsf.fi/publ/foregsatlas/) (Table 2).

Table 2: Range in background Sb concentrations in water, sediment and soil (from FOREGS).

	Minimum	10^{th} percentile	Median	90^{th} percentile	Maximum	PNEC
Stream water (µg/L)	<0.002	0.01	0.07	0.21	2.91	113
Stream sediment (mg/kg dry weight)	<0.02	0.22	0.62	2.10	34.1	11.2
Topsoil (mg/kg dry weight)	0.02	0.15	0.60	1.91	31.1	37
Subsoil (mg/kg dry weight)	<0.02	0.11	0.47	1.53	30.3	37

Metals are obviously persistent in the sense that they do not degrade to CO_2, water, and other elements of less environmental concern. As a consequence, it has been argued that traditional persistence measures used for organic substances do not equally apply to metals (Adams et al. 2000). While it is recognized that metals are conserved, the form and availability of the metal can change and the persistence of the bioavailable species is the more appropriate hazard indicator for metals.

This potential transformation of metal species to non-bioavailable forms through complexation, precipitation, adsorption, and settling is recognized in Annex IV of Guidance to Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of substances and mixtures. For soluble metal species, a rapid removal definition based on laboratory, mesocosm, and/or field data tests has been proposed. The term "Rapid removal" is a more accurate description for metals in this respect, because, partitioning (e.g. by precipitation and especially speciation processes) can lead to the non-available form and the elimination of metals from the water column. However, caution is advised given the possibility that 1) these processes do not necessarily reduce bioavailability and/or 2) the reduction in bioavailability afforded by these processes is not necessarily permanent. In accordance with the principles of rapid removal used for organic substances rapid removal can be defined for metals as a reduction of the soluble metal species by > 70% in 28 days. Furthermore, the potential for remobilization from the sediment must be negligible.

A preliminary assessment on the removal of Sb from a water column based on the standard lake as defined in EUSES model (suspended solids: 15 mg/L; depth: 3 m; settling rate: 2.5 m/d and residence time 40 days) and a constant partition coefficient for Sb to suspended matter (log Kp = 3.65 l/kg; ECB, 2008; ECHA, 2010) is shown in Figure 1. This assessment does not take into account potential remobilisation of Sb from the sediment due to e.g. resuspension or diffusion. In oxic sediments, Sb is mainly adsorbed onto iron and manganese oxides. In anoxic sediments, and in the presence of sulfur, depending on pH, antimony forms soluble or insoluble stibnite, SbS_2^- and $Sb_2S_3(s)$, respectively. This may result in a further decrease in bioavailable antimony, as compared to the oxic part of the sediment. Based on a log Kp of 3.65 l/kg, it is predicted that 6.3% of the total Sb in the water column is adsorbed on the suspended matter. Partitioning and settling reactions result in 70% removal of the dissolved Sb concentration from the water column after approximately 15 days. It must be noted however, that these results are strongly dependent on the input parameters (Kp, settling rate etc.). A settling rate of 0.5 m/d will e.g. result in only 65% removal within 28 days. No further correction for speciation of the dissolved Sb species is included because toxicity data for aquatic organisms are all based on total dissolved Sb concentrations.

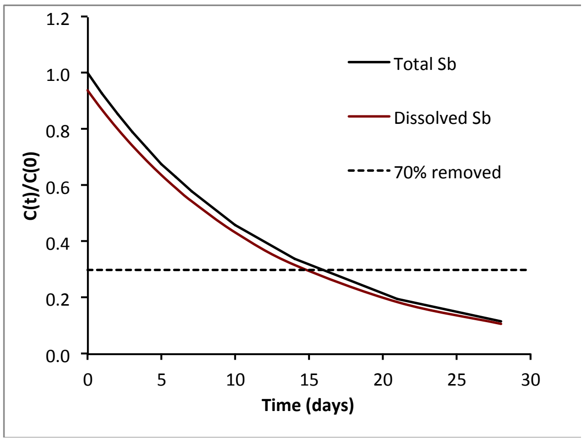

Figure 1: Total and dissolved Sb removal from the water column using EUSES standard lake parameters and a constant log Kp of 3.65 l/kg).

Conclusion

In conclusion, whereas antimony formally meets the criterion for persistence based on the absence of any degradation, this criterion is considered not to be applicable to inorganic elements. In addition, under conditions of a standard EUSES lake and the median partition coefficient for suspended matter, Sb meets the criteria for rapid removal from the water column.

Bioaccumulation

Bioaccumulation is the process whereby aquatic organisms accumulate substances in their tissues from water and diet. Bioaccumulation is of potential concern both because of the possibility of chronic toxicity to the organisms accumulating substances in their tissues and because of the possibility of toxicity to predators eating those organisms.

Some metal-specific considerations need to be made on the concept of bioaccumulation. Due to their natural occurrence, biota will naturally accumulate metals at least to some degree without deleterious effect (ICMM, 2007). For most metals and inorganic metal compounds the relationship between water concentration and BCF in aquatic organisms is inverse, and bioconcentration data are therefore often not reliable predictors of chronic toxicity or food chain accumulation in the aquatic environment. Unlike organic substances, which may be taken up by passive diffusion across cell walls, the uptake and removal processes of essential elements are actively regulated in order to maintain a reasonable constant internal concentration (homeostasis). Also non-essential metals are actively regulated to some extent and therefore also for non-essential metals, an inverse relationship between the metal concentration and the external concentration may be observed (Mc Geer et al., 2003). Assessing bioconcentration factors for metals should therefore preferably be done from BCF studies using environmentally relevant concentrations in the test media. Further, inorganic elements are no hydrophobic (lipophilic) organic chemicals and would therefore, not be expected to accumulate in lipid to a greater extent than in non-lipid tissues and consequently, BCF values for metals should not be lipid normalised.

There are no BCF values available from standard laboratory studies designed to measure the bioaccumulation of antimony. In the EU Risk Assessment Report and the REACH dossier of Sb_2O_3, tentative bioconcentration factors were estimated using results from monitoring studies where the concentration of antimony has been measured in different aquatic organisms and other studies, which have reported typical background levels of antimony in the water (ECB, 2008; ECHA, 2010). Only two studies have been reported with levels of antimony from both the water and organisms and BCF data were only available for exposure concentrations in water up to 3.1 µg Sb/l, much below the PNEC for Sb in fresh- or marine water (respectively 113 and 11.3 µg/l). The highest tentative BCF values reported for antimony are all for marine algae, with the highest value being 114 l/kg dry weight. Only one study allows for correction of background concentrations in water and organisms and reports a BCF value of 56 l/kg dry weight for the invertebrate *Hyalella azteca* for an exposure concentration of 0.5 µg Sb/l, while BCF values of >800 l/kg dry weight were observed in controls (Couillard et al., 2008).

There have been few studies that have evaluated the biomagnification potential of antimony within food chain webs. Available studies (Campbell et al. 2005, Ikemoto et al. 2008) did not necessarily assess real trophic linkages, but have found no evidence for the biomagnification of antimony whilst at the same time finding evidence of the biomagnification of mercury. There is therefore no evidence to suggest that antimony is likely to biomagnify within food chains.

Conclusion

Antimony does not meet the criteria for bioaccumulation because the BCF values reported for aquatic organisms are all much lower than the threshold of 2,000 l/kg, and there is evidence to support that antimony does not biomagnify in the food chain.

Toxicity

Reliable chronic ecotoxicity test data are available for the effects of $SbCl_3$ and Sb_2O_3 on freshwater fish, invertebrates, and algae. All results are expressed based on dissolved elemental Sb concentrations. The chronic no observed effect concentration (NOEC) values obtained from reliable and relevant tests are all above 1 mg Sb/l. The most sensitive result from a chronic ecotoxicity test was derived from a 28-day study with $SbCl_3$ on the length of the fathead minnow (*Pimephales promelas*) and resulted in a 28 day NOEC value of 1.13 mg Sb/l (Kimball 1978). This is a factor 100 above the threshold value of 0.01 mg/l for PBT assessment. As these ecotoxicity tests have tested the toxicity of dissolved antimony, this assessment is also considered to apply to antimony from other antimony containing substances when dissolved in water.
The Predicted No Effect Concentrations (PNEC) for inorganic Sb in fresh- and marine water are 0.113 and 0.0113 mg Sb/l, respectively. PNEC values for freshwater and marine sediments and soil are 11.2, 2.24 and 37 mg Sb/kg dry weight, respectively. These PNEC values for water and soil are above the range in natural background concentrations observed across Europe, while for

freshwater sediment less than 1% of the sites have a natural background concentration above the PNEC value (Table 2).

Antimony trioxide is classified R40 (limited evidence of a carcinogenic effect) or H351 (Suspected of causing cancer by inhalation), and therefore, considered to be a category 3 inhalation carcinogen according to 67/548/EEC (Dangerous Substance Directive) or an inhalation Carcinogen Class 2 (1272/2008/EC). Antimony trioxide is indeed an inhalation carcinogen for female rats, but the mechanism for cancer is unspecific and related to particle overload with inert poorly soluble particles (PSPs). The relevance for humans is unclear, and occupational inhalation exposure is the only relevant human exposure pathway. Yet, workers are adequately protected to ensure that occupational exposure does not exceed the Occupational Exposure Limits (OELs) of 0.5 mg Sb/m^3.

Conclusion

Antimony does not meet the PBT criteria for toxicity.

Overall conclusions

There is sufficient information available on the behaviour and toxicity of Sb to perform a PBT assessment. Antimony does not meet the criteria for bioaccumulation and toxicity. Whereas it formally meets the degradation-based criterion for persistence, the latter cannot be considered applicable to inorganic elements. In addition, under conditions of a standard EUSES lake and the median partition coefficient of Sb for suspended matter, Sb meets the criteria for rapid removal from the water column.
It is therefore concluded that antimony and inorganic antimony compounds are neither a PBT substance, nor a vPvB substance.

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