

Aluminium Silicate (Kaolin)

DOCUMENT M-CA, Section 7

FATE AND BEHAVIOUR IN THE ENVIRONMENT

Annex to EU Regulation 283/2013

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¹ It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report

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CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

This dossier refers to calcined kaolin, registered in 2008 under the term "Aluminium silicate". The regulatory term used throughout this dossier is therefore aluminium silicate, although in geological and mineralogical terms, the substance described therein is known as calcined kaolin.

The kaolin clay which is the subject of this Active Ingredient Renewal dossier originates exclusively from the state of Georgia, United States of America. Therefore, **some of the geological information presented below originates from local (Georgia, USA) historical sources and should not be used to evaluate the characteristics and properties of aluminium silicate (kaolin) originating from other geological areas, such as Asia or Europe.**

A waiver is requested for all fate and behaviour in soil data. A reasoned argument as to why a waiver is justified is presented below that is expected to **satisfy every data point.**

Due to the industrial and commercial importance of aluminosilicate minerals, the formation and transformation of clay minerals has been studied for centuries. The volume of geological, mineralogical and environmental data on aluminium silicates, clays and kaolin is such that an exhaustive presentation of the published literature is outside the scope of this dossier. Nevertheless, information from published textbooks, articles and reference material is presented herein to demonstrate **why the fate and behaviour of aluminium silicate (kaolin) in soil cannot be assessed under the framework of Regulation (EC) 1107/2009 nor Regulation (EU) 283/2013.**

CA 7.1 Fate and Behaviour in Soil

Reference:	KCA 7/01, Veatch O., McCallie S.W., 1909
Title:	Geological survey of Georgia, Bulletin n°18, Second report on the clay deposits of Georgia
Report No.:	Not applicable
Guideline(s):	Not applicable
Deviation(s):	Not applicable
GLP:	No

Origin and age of Kaolin deposits in Georgia, USA:

Chapter 1, pp. 17-18:

"All clays are of secondary origin and have been derived directly or indirectly from the decay and breaking down of the original igneous rocks or the earth's crust. This decay has taken place mainly through the atmospheric agencies, rain, frost, changes in temperature, wind, and through atmospheric gases and organic agencies, plants and animals, all of which may be included under the term weathering. The minerals of igneous rocks, which have been the chief source of kaolinite, or the clay base or clay substance of clays, are the feldspars. Other aluminous minerals, however, have doubtless been a source of the kaolinite of clays, and the following list of minerals has been noted by Prof. C. R. Van Hise as having produced kaolinite through chemical alteration: Andalusite, anorthoclase, biotite, cyanite, epidote, leucite, microcline, nephelite, orthoclase, plagioclase, scapolite, sillimanite, sodalite, topaz and zoisite."

Aluminium silicate (kaolin), like other clays, is therefore a by-product of natural erosion of rocks.

Chapter 4, p. 65:

*"The clays of Georgia of commercial value have a wide geological distribution, ranging from the **pre-Cambrian** igneous and metamorphic rocks to the alluvial deposits of the **Pleistocene**."*

Therefore, aluminium silicate deposits mined today range from > 600 million years-old (pre-Cambrian) to > 1 million years old (Pleistocene).

Therefore, assessing the route and rate of degradation of aluminium silicate under the required framework would not contribute to the regulatory database, nor be practical, as the presence of aluminium silicate (kaolin) is measured in millions of years. **Aluminium silicate (kaolin) does not degrade at human timescales.**

~~Aluminium silicate is insoluble, photolytically stable and inert even to mineral acids and bases, except under very harsh conditions. Aluminium silicate has a similar chemical composition to common clay that is found in most soils and aquatic sediments the world over. No increase in compaction, water penetration or aeration is anticipated since the existing clay particles exist in a much larger particle size distribution (already agglomerated) than the narrow fraction that will be added. Expectations are that by using kaolin instead of another pesticide having toxic residues, the soil biodiversity will improve under Surround treated fields, since none of the present organisms would be exposed to additional potential toxins.~~

~~Since aluminium silicate is a non-degradable natural component of the environment a waiver is requested for all environmental fate studies.~~

CA 7.1.1 Route of degradation in soil

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.1.1 Aerobic degradation

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.1.2 Anaerobic degradation

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.1.3 Soil photolysis

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.2 Rate of Degradation in Soil

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.2.1 Laboratory studies

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.2.1.1 Aerobic degradation of the active substance

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

CA 7.1.2.1.3 Anaerobic degradation of the active substance

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

CA 7.1.2.2 Field Studies

Not applicable, aluminium silicate does not degrade in soil. See Point CA 7.1 for waiver request.

CA 7.1.2.2.1 Soil dissipation studies

CA 7.1.2.2.2 Soil accumulation studies

CA 7.1.3 Absorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

CA 7.1.3.1.1 Adsorption and desorption of the active substance

Not applicable.

A waiver is requested for adsorption and desorption data on aluminium silicate (kaolin).

Aluminium silicate (kaolin) is essentially purified natural clay and is therefore not subject to adsorption on or desorption from soil particles, as it is a component of said soil particles. Aluminium silicate (kaolin) particles will readily mix with the other soil components. Some organic materials (for example fulvic acids) will adsorb onto the particle surfaces, similarly to the aluminium silicate (kaolin) already existing in the soil. Adsorption and desorption of aluminium silicate (kaolin) to soil contaminants is therefore well described in regulatory evaluation dossiers as all adsorption/desorption studies involving standard soils will involve aluminium silicate as a soil component.

This is exemplified in OECD Guidance n°106, Adsorption - Desorption Using a Batch Equilibrium Method.

In this guidance, paragraph 7 states: "The soil parameters that are believed most important for adsorption are: organic carbon content [references]; clay content and soil texture [references]; and pH for ionisable compounds [references]."

Paragraph 18 of OECD Guidance n°106 also states: "The soils should be characterised by three parameters considered to be largely responsible for the adsorptive capacity: organic carbon, clay content and soil texture, and pH. As already mentioned in paragraph 7, other physico-chemical properties of the soil may have an impact on the adsorption/desorption of a particular substance and should be considered in such cases."

OECD Guidance n°106 also provides guidance for the selection of soils based on pH range, organic carbon, clay content and soil texture:

Table 1: Guidance for selection of soil samples for adsorption-desorption

Soil type	pH range (in 0.01 M CaCl ₂)	Organic carbon content (%)	Clay content (%)	Soil texture*
1	4.5-5.5	1.0-2.0	65-80	clay
2	> 7.5	3.5-5.0	20-40	clay loam
3	5.5-7.0	1.5-3.0	15-25	silt loam
4	4.0-5.5	3.0-4.0	15-30	loam
5	< 4.0-6.0 [§]	< 0.5-1.5 ^{§‡}	< 10-15 [§]	loamy sand
6	> 7.0	< 0.5-1.0 ^{§‡}	40-65	clay loam/clay
7	< 4.5	> 10	< 10	sand/loamy sand

* According to FAO and the US system (85).

§ The respective variables should preferably show values within the range given. If, however, difficulties in finding appropriate soil material occur, values below the indicated minimum are accepted.

‡ Soils with less than 0.3% organic carbon may disturb correlation between organic content and adsorption. Thus, it is recommended the use of soils with a minimum organic carbon content of 0.3%.

The generic term "clay" is not defined in the guidance; a definition of "clay" is provided in Bergaya et al. (Ed), Handbook of Clay Science, 1st Edition, Development in Clay Science 1, Elsevier Ed. 2006.

Chapter 1, pp. 3-5 states: "*There is, as yet, no uniform nomenclature for clay and clay material. Nonetheless, we do not seek a consensus about the meaning of the terms 'clay', 'clays', and 'clay minerals' [...]. Georgius Agricola (1494–1555), the founder of geology, was apparently the first to have formalized a definition of clay (Guggenheim and Martin, 1995). The latest effort in this direction was made nearly five centuries later by the joint nomenclature committees (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS). The JNCs have defined 'clay' as "...a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with (sic) dried or fired" (Guggenheim and Martin, 1995). [...] Although particle size is a key parameter in all definitions of clay, there is no generally accepted upper limit. Some disciplines and professions, however, have conventionally set a maximum size of clay particles. In pedology, for example, the 'clay fraction' refers to a class of materials whose particles are smaller than 2 µm in equivalent spherical diameter (e.s.d.). In geology, sedimentology, and geoengineering the size limit is commonly set at 0.4 µm e.s.d. (Moore and Reynolds, 1997), while in colloid science the value of 0.1 µm is generally accepted. Indeed, Weaver (1989) has suggested that the term 'clay' should only be used in the textural sense to indicate material that is finer than 4 µm.*"

Under these criteria the active substance Aluminium silicate (kaolin), which presents a particle size within the range of 0.7 to 11 µm (CP 2.8.5.1, particle size distribution, in Miller 2012¹, report number ARC-EX-848-012-P-1) is clearly a clay.

Under those circumstances, adsorption and desorption testing with aluminium silicate (kaolin) is meaningless as the test would involve adding clay to soil, rather than adding an organic substance capable of interacting with the test medium.

¹ Study performed on the example formulation, a wettable powder containing 95% w/w Aluminium silicate (kaolin)

Expectations are that by using kaolin instead of another pesticide having toxic residues, the soil biodiversity will improve under aluminium silicate treated fields, since none of the present organisms would be exposed to additional potential toxins.

CA 7.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

Not applicable. Aluminium silicate is not metabolised and does not degrade or react. Please refer to Point 7.1 for waiver request. Aluminium silicate is stable.

CA 7.1.3.2 Aged sorption

Not applicable. Please refer to Point CA 7.1.3.1.1. for waiver request.

CA 7.1.4 Mobility in soil

Not applicable. Aluminium silicate is not mobile. When applied to soil, aluminium silicate particles will readily mix with other soil components and remain in the topsoil unless physically mixed with the subsoil layer. **Therefore, a waiver for mobility studies is requested.**

The mobility of clay particles in soil has not been investigated because because clays such as aluminium silicate (kaolin) are known to be insoluble in water, as demonstrated in the presence of an impermeable clay layer in most ponds, lakes or reservoirs. Therefore, aluminium silicate (kaolin) cannot be transported as solute through the soil layer.

Numerous literature sources refer to the clay content expected in soils in general and agricultural soils in particular, such as Newman A.C.D, The significance of clays in agriculture and soils, *Phil. Trans. R. Soc. Land. A* 311, 375-389 (1984) states (pp. 155-156):

"A soil usually contains at least some clay, and its clay content strongly influences its management and productivity (Davies et al. 1972). Soils with very little clay can be just as difficult to manage, for different reasons, as soils that contain large amounts, and in broad terms loam soils containing 15- 25% clay with particle sizes of under 2 µm and a larger proportion of silt particles sized 2-60 µm are the most productive. Such soils seem to contain enough clay to provide an adequate surface for interaction with water and nutrients, and to have a friable structure beneficial for tillage and root growth. Soils with more than 30-35 % by mass weight of clay tend to take on the properties of the clay itself, with the implications that they waterlog more easily during periods of excess rainfall, stay wet longer, require greater draft in cultivation and form large aggregates (clods) that must be broken down to form a favourable seed bed. In short, they pose more management problems than loamy soils."

Despite these apparently unfavourable properties conferred on soils by an excess of clay, clay makes a vital contribution to soil fertility. In combination with organic matter and sesquioxides, clay contributes coherence and structural stability which enables the soil to resist the mechanically destructive effects of rain and wind. Because clays have a large specific surface that is predominantly negatively charged, they retain cationic nutrients like K^+ and NH_4^+ , and also absorb toxic substances. Layer silicate clays may also have plant nutrients present in their structure, and K^+ and Mg^{2+} can be released to soil solution under appropriate conditions."

CA 7.1.4.1 Column leaching studies

Waiver request. Not applicable. Please refer to Point CA 7.1.4.

CA 7.1.4.1.1 Column leaching of the active substance

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

CA 7.1.4.2 Lysimeter studies

Waiver request. Not applicable. Please refer to Point CA 7.1.4.

CA 7.1.4.3 Field leaching studies

Waiver request. Not applicable. Please refer to Point CA 7.1.4.

CA 7.2 Fate and Behaviour in Water and Sediment

Waiver request. Not applicable.

Aluminium silicate is extremely stable. Aluminium silicate is insoluble, photolytically stable and inert even to mineral acids and bases. Aluminium silicate has similar chemical composition to common clay that is found in most soils and aquatic sediments the world over. Since aluminium silicate is a non-degradable natural component of the environment a waiver is requested for all environmental fate studies.

The following reference discusses settling behaviour of clays when water with natural clay from estuaries and deltas enters marine water. Although the experiments described herein focus on saltwater sedimentation, insight on the behaviour of clay particles in fresh water is also provided.

Reference:	KCA 7.2/01, Sutherland B.R. et al, 2014
Title:	Clay settling in fresh and salt water, Environ Fluid Mech, volume 15, Issue 1, pp 147–160
Report No.:	Not applicable
Guideline(s):	Not applicable
Deviation(s):	Not applicable
GLP:	No

Materials and methods

A specified mass of clay is suspended in a fixed volume of water and settling of the particles is observed over time by means of a photographic camera.

Test material: K-WHITE 5000, calcined aluminium silicate powder [45 (±2) % Al₂O₃ and 52 (±2) % SiO₂] from American Elements. Referred to hereafter as “KW5000 clay”, 90 % of the powder consisted of particles with size near 2 µm with <0.005 % of the particles having size above ~45 µm.

Test material concentration: between 15 and 40 ppt by weight (15 to 40 µg/kg).

The KW5000 clay powder was added to the water in the tank and the water was stirred vigorously with a mixer until the mixture was uniform. The stirrer was then extracted and this was taken to

be the start time ($t = 0$) of experiments. To examine the effect of particle consolidation and possible de-gassing of the particles, in some experiments the clay was allowed to settle overnight and then the mixture was re-stirred.

Results and discussion:

Figure 2 shows snapshots and vertical time series constructed from four experiments with KW5000 clay settling in fresh and salt water. In Fig. 2a, clay added to fresh water remained well suspended even after 25 min. This is apparent because the intensity of light passing through the tank changed little over time from top to bottom. Experiments of this type which were conducted for long periods showed that it took over 10 h before all the clay had settled to the bottom 1 cm of the tank. This is consistent with the settling time predicted for individual spherical particles of radius $r_p = 1 \mu\text{m}$ and density $\rho_p = 2 \text{ g/cm}^3$ to fall $H = 10 \text{ cm}$ at the Stokes settling velocity,

$$w_s = \frac{2}{9} \frac{g' r_p^2}{\nu} \quad (1)$$

in which $g' = g(\rho_p - \rho_w)/\rho_w$ is the reduced gravity, and $\rho_w = 0.9982 \text{ g/cm}^3$ and $\nu = 0.01 \text{ cm}^2/\text{s}$ are respectively the density and kinematic viscosity of fresh water at room temperature. Explicitly, we estimate $w_s \approx 2 \times 10^{-4} \text{ cm/s}$, which gives a setting time of $H/w_s = 5 \times 10^4 \text{ s} \approx 13 \text{ h}$.

Figure 2c shows the results of an experiment in which KW5000 clay was allowed to settle overnight in fresh water before being remixed. Here a fraction of the particles are observed to settle out in the first 10 min of the experiment. Presumably, these were particles that formed flocs while consolidating at the bottom of the tank. However, a substantial fraction of the clay particles remained in suspension even after 25 min, as evidenced by the relatively low intensity of light passing through the tank even near the surface.

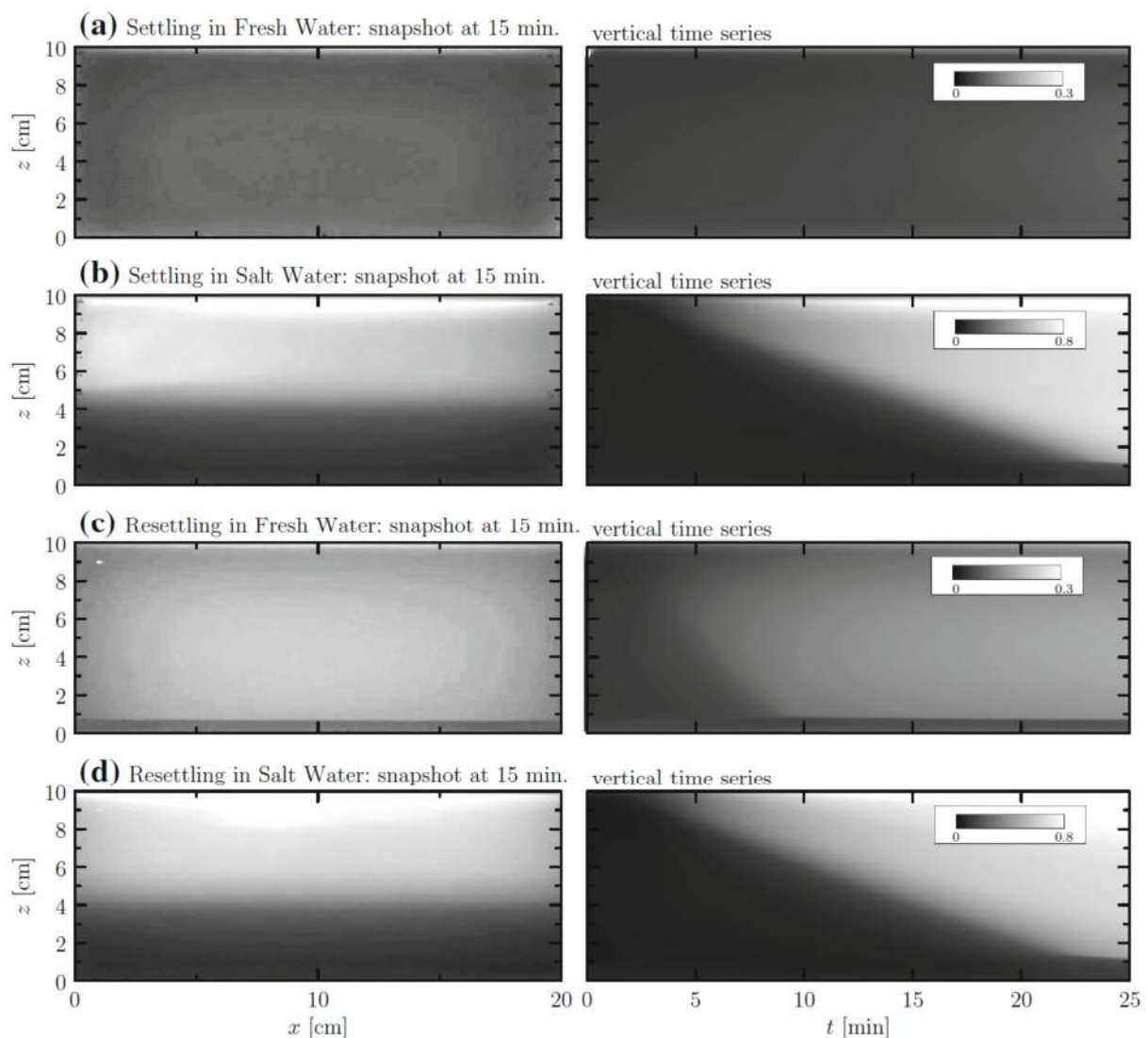


Fig. 2 Snapshots after 15 min (*left column*) and vertical time series of along-tank-averaged light intensity (*right column*) taken from experiments with 14.7 ppt KW5000 clay settling in fresh and salt water: **a** dry clay mixed with fresh water, **b** dry clay mixed with 5 psu saline water (11.0g NaCl added to tank), **c** clay in fresh water settles 20 h and is then remixed before start of experiment, **d** after this experiment, 11.0g NaCl added to tank and the 5 psu saline water is mixed with resuspended clay before start of experiment. The gray scale for intensity in each snapshot and corresponding time series is indicated in the *top-right* of each time series plot. Note the intensity of light passing through the tank is significantly brighter near the surface in the salt-water experiments (time-lapse movies of these experiments can be viewed as supplemental material)

Conclusion:

Clay may settle quickly in fresh water if it has already undergone processes that permit the formation of large flocs.

Discussion on the applicability of this article with regards to the fate and behaviour of aluminium silicate (kaolin) in water and sediment

The test material used in this article is similar to the active ingredient aluminium silicate (kaolin) in terms of quality (kaolin clay, calcined aluminium silicate powder) and particle size (90% around 2 µm when the representative product contains 90% of particles around 6 to 7 µm).

The principal elements one can infer from this article from an environmental fate perspective are:

- Aluminium silicate (kaolin) does not dissolve nor degrade in fresh or salt water, therefore no further testing is necessary;
- Aluminium silicate (kaolin) is naturally present in riverine sediment;
- Aluminium silicate (kaolin) will settle more readily when particles have already agglomerated in water and are re-suspended,

This latter point is particularly important with regard to the application of aluminium silicate (kaolin) on crops. SURROUND® WP CROP PROTECTANT is a wettable powder, designed for application following suspension in water. Thus, the calcined kaolin particles that compose 95% of the representative product will be subjected to agglomeration when suspended in the spray prior to application to the crop. Therefore, settling of the particles will be comparatively more rapid than that reported for the test material in the reported article.

CA 7.2.1 Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.1.1 Hydrolytic degradation

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.1.2 Direct photochemical degradation

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.1.3 Indirect photochemical degradation

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.2.1 “Ready biodegradability”

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.2.2 Aerobic mineralisation in surface water

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.2.3 Water/sediment studies

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.2.4 Irradiated water/sediment study

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.2.3 Degradation in the Saturated Zone

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.3 Fate and Behaviour in Air

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.3.1 Route and rate of degradation in air

Waiver request. Not applicable. Please refer to Point CA 7.2.

CA 7.3.2 Transport via air

Waiver request. Aluminium silicate particles are identical to natural clay particles and may be transported via air as common dust. Once airflow is sufficiently low, particles will settle on soil and become indistinguishable from naturally present soil particles.

CA 7.3.3 Local and global effects

Waiver request. Not applicable. Aluminium silicate is akin to common clay and as such may be displaced by wind and redeposited on soil and other surfaces, where it becomes indistinguishable from naturally present soil particles.

CA 7.4 Definition of the Residue

Waiver request. Not applicable. Aluminium silicate is a natural component of all agricultural soils and applied aluminium silicate will be indistinguishable from naturally present clay. Therefore, the concept of residue in the environment does not apply to aluminium silicate.

CA 7.4.1 Definition of the residue for risk assessment

Not applicable. Please refer to Point CA 7.4.

CA 7.4.2 Definition of the residue for monitoring

Not applicable. Please refer to Point CA 7.4.

CA 7.5 Monitoring Data

Waiver request. Not applicable. Aluminium silicate is a natural component of all agricultural soils and applied aluminium silicate will be indistinguishable from naturally present clay. Therefore, the concept of residue in the environment does not apply to aluminium silicate.