Ferric pyrophosphate

Volume 3

Active substance data

Annex B.8: Environmental fate and behaviour

Rapporteur Member State: Poland
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Volume 1

Level 1: Statement of subject matter and purpose for which the monograph was prepared

Level 2: Reasoned statement of the overall conclusions drawn by the Rapporteur Member State

Level 3: Proposed decision with respect to the application

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List(s) of endpoints

List of endpoints

Version history

Date	Reasons for revision
July 2019	1st RAR update. All new data and changes are highlighted in yellow.
November 2019	2nd RAR update. All new data and changes are highlighted in green.

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B.8 Fate and Behaviour in the Environment

B.8.1 Fate and Behaviour in Soil

Active substance – ferric pyrophosphate – is a stable non-volatile inorganic salt, virtually insoluble in water. On the other hand, it may undergo dissociation reactions in soil to transform into its corresponding Fe^{3+}/Fe^{2+} and $P_2O_7^{4-}$ ions, which naturally occur in both the terrestrial and aquatic environmental compartments.

Iron

Iron is a commonly occurring metallic element, the second most abundant metal in the natural environment and the fourth most abundant element, which composes about 5% of the Earth's crust, mostly in the form of ferromagnesium silicates, with soils typically containing 1 – 5 % total iron (Draggan, 2011, Schulte, 1992). It is also found in the environment in the form of minerals such as: hematite, magnetite, siderite or pyrite. The silicate minerals or iron oxides found in the soil are not readily available for plant use. In terms of ferric ions in soil, the soil pH and the aeration status of the soil determines which form (ferric or ferrous) predominates, nevertheless, it is expected to be primarily Fe^{3+} (ferric). As discussed in the EFSA (2015) conclusion for ferric phosphate, during heavy rainfall, the soil environment may become anaerobic leading to the formation of Fe^{2+} ions. Reactions with organic matter also influence iron availability.

The content and distribution of iron in soils varies significantly even within localized areas, due to soil types and the presence of other sources; different sources indicate different values from 0.2% to 55% (20,000 to 550,000 mg/kg); typically 1–5% (10 – 50 g/kg). Iron comprises 4.6% of igneous rocks and 4.4% of sedimentary rocks. Iron can occur in either the divalent (ferrous or Fe^{+2}) or trivalent (ferric or Fe^{+3}) states under typical environmental conditions. The valence state is determined by the pH and Eh (redox potential) of the system, and the iron compound is dependent upon the availability of other chemicals (e.g., sulfur is required to produce FeS_2 or pyrite) (US EPA, 2003).

Based on of the RAR for ferric phosphate the natural occurrence of iron in soils is 2 to 50 g/kg soil.

The Fe_2O_3 content in subsoil is low (<2.40%) throughout the glacial drift sandy plains from Poland to the Netherlands, much of the Baltic states, large parts of southern Finland and Sweden, and limestone areas in southern Spain and north-central France. In turn, the Fe_2O_3 content in subsoil is high (>5.44%) in north-western Spain (mafic and ultramafic lithologies of the Ordenes ophiolite), the western Pyrenees (siderite replacement deposits in Lower Cretaceous), Brittany, Central Massif (soil over Quaternary basalt), a north-south band in Italy from north of the Garda Lake to the Roman Alkaline Province, southern Sicily, Greece

north of the Gulf of Corinth (terra rossa soil, ophiolite, bauxite, Fe-Ni mineralisation), Croatia, Slovenia and southern Austria (karstic residual soil), eastern Slovakia (soil over volcanic rocks and Palaeogene flysch with ultramafic clasts), eastern Latvia (related to iron concretions due to changes in oxidation-reduction conditions close to groundwater level in poorly drained soil), parts of Norway (amphibolite), the ice divide area of northern Finland (which is rich in mica), the west coast of Wales and Scotland, and northern Ireland (over the Antrim basalt). What most of these areas have in common is crystalline rocks of intermediate to mafic or alkaline affiliation, including greenstone belts, and also karst with soils on carbonate rocks (Greece, Croatia, Slovenia). In northern Finland iron ores are present, and magnetite has a tendency to be enriched during weathering. Weaker iron enrichment occurs in southern Portugal, and the French-Belgian Ardennes and parts of central England where Mesozoic red-beds and sedimentary iron ores are present (Salminen et al., 2005).

Heavy soils might sometimes contain twice as much iron as sandy soils. Most of the iron in soil is found in silicate minerals or iron oxides and hydroxides, forms that are not readily available for plant use. Examples of iron phosphates found in soil are vivianite, stable in anaerobic conditions ($Fe_3(PO_4)_2$ x 8 H_2O) and strengite, stable in acidic soils ($FePO_4$ x 2 H_2O). Iron is one of the most mobile elements in soil and in unfavourable conditions it very fast moves deep into the soil profile, which decreases the amount of forms readily available for plant use. Iron compounds are released as a result of soil or rock weathering. Under typical environmental conditions, the element is found in two oxidation states - reduced, as ferrous iron Fe^{2+}, or oxidized, as ferric iron Fe^{3+}. Even though most of iron in the Earth's crust has the ferric form Fe^{3+}, it is the ferrous form Fe^{2+} that is more physiologically important for plants. This form is relatively soluble but it is readily oxidized to Fe^{3+}, which in turn precipitates as very insoluble oxides and hydroxides and thus becomes inaccessible to plants. Soil pH and the aeration status of the soil determine which form predominates. Ferric iron compounds Fe^{3+} have low solubility in the soil solution, and conditions that favour formation of these compounds decrease iron availability. The concentration of iron in the soil solution decreases sharply as the soil pH increases. Iron content in edible plant organs is 10 – 320 mg/kg of dry weight. The element is essential for the production of chlorophyll, it is found in certain proteins and takes part in the process of cellular respiration. Deficiency symptoms, manifested as leaf chlorosis, appear first on the youngest leaves but with time they can also affect older leaves. To cope with low iron availability in soil, plants have developed various mechanisms for iron acquisition. One of them is excreting hydrogen ions H^+ from roots, which lowers the pH at the root surface and increases the solubility of iron. Another mechanism is the release of ferric ion chelating agents – siderophores – which by forming complexes with Fe^{3+}, increase their solubility. Several factors reduce the bioavailability of Fe, including high soil pH, high bicarbonate content, plant species (grass species are usually more efficient than other species because they

can excrete effective ligands), and abiotic stresses. Plants typically utilize iron as ferrous iron (Fe^{2+}). Ferrous iron can be readily oxidized to the plant-unavailable ferric form (Fe^{3+}) when soil pH is greater than 5.3. Iron deficiency often occurs if soil pH is greater than 7.4. Chelated iron can prevent this conversion from Fe^{2+} to Fe^{3+}. (Liu et al., 2012).

Iron was also among the very first elements to be identified as essential nutrients for plants. Soils rarely contain less than 0.7% Fe by weight. Thus a 50-cm layer of soil contains at least 40,000 kg Fe per hectare. The soil solution in a 50-cm layer of 1 ha of cultivated soil (assuming water content of 40% by volume) with Fe concentration of 10^{-10} M, contains as little as 10 mg Fe. A pH range of 7.4 to 8.5, in which inorganic forms of Fe are at minimal concentration, is common to calcareous soils, which cover over 30% of the Earths land surface, especially in arid and semi-arid regions. Diffusion of Fe in the solution towards active sites of uptake in the roots might partially bridge the wide gap between the amount of Fe needed and the Fe available, and indeed it was found to be a principal means for Fe movement in soil towards plant roots (Chen & Shenker, 2004). As a source of iron in plant fertilization, fertilizers containing iron in the chelated form are used. The mineral form ($FeSO_4$ x $7H_2O$) with a 20.2% Fe is used in the fertilization of field crops and for traditional substrates used in indoor application. Usually the entire dose is introduced before vegetation, bringing the content of iron up to 50 mg Fe/L of the substrate, and this should be enough for the entire growing season. In the farming system with fertigation, iron content in the medium should be maintained at 1-2 mg Fe/L using chelate fertilizers. In systems with drip irrigation, only this form of this microelement is recommended, otherwise the ferric hydroxide may clog the capillaries (Chohura, 2005, Fruzinska, 2011).

In agriculture, several chelating agents are allowed for use, e.g. EDTA, which prevents the conversion of Fe^{2+} to Fe^{3+}. Doses of chelated fertilizers containing 6-12% Fe suggested by the manufacturers are usually about 0.6 – 2.2 kg of iron/ha. Approximate doses of fertilizer containing 6-7% Fe, recommended in garden plant cultivation are as follows: 0.6 kg Fe/ha as preventive measure, 3 kg Fe/ha in the case of moderate deficiency and 6 kg Fe/ha in the case of serious deficiency.

Phosphorus

Phosphorus is the eleventh most abundant element in the Earth's crust, constituting approximately 0.1% by weight. It is an abundant non-metallic element and exhibits lithophile, siderophile and biophile properties depending on the circumstances. It occurs almost exclusively in nature as orthophosphate ($PO4^{3-}$), principally in the mineral apatite $Ca_5(PO_4)_3(F, Cl, OH)$, but also in monazite (Ce, La, Nd, Th,

Sm)(PO_4,SiO_4) and xenotime YPO_4. Phosphorus belongs to the volatile components of magmas, although great variation of P levels are found in magmatic rocks, even with rocks of a similar type; the average concentrations of P in various rock types as: ultramafic 220 mg/kg; basaltic 1100 mg/kg; granitic 600–920 mg/kg, with a crustal average of 1120 mg/kg. Data on abundances for P in metamorphic rocks are rare, but there is a trend of increasing P content with increasing metamorphic grade. The amount of P in clastic rocks depends on their origin and grain size, with the P content generally increasing with decreasing grain size. Levels in shale are reported as 700 mg/kg; sandstone 170 mg/kg, and carbonate rocks 400 mg/kg. Although they are rare, sedimentary bone beds contain abundant fossil phosphate, and high levels are also found in organic-rich black shale where Fe phosphate and U often occur together. The solubility of apatite and Fe-Al phosphate and the adsorption of phosphate on clay minerals are the two most important factors in the weathering of minerals containing P. In acid environments, apatite is remarkably soluble, as HPO_4^{2-} and H_2PO^{4-} ions formed by the equilibrium reaction of H^+ with PO_4^{3-} are soluble in the presence of Ca^{2+}. In neutral and alkaline conditions, calcium orthophosphate is largely insoluble. Except in very acid conditions (pH<3.0), Al and Fe phosphates are highly insoluble, and their formation limits the mobility of P in soil and stream sediment. In soil, P also forms low solubility minerals with Pb and Ca, such as plumbogummite and pyromorphite, which are even less soluble than common Ca-phosphates. The sorption of phosphate to alumino-silicate clays and hydrous oxides of Fe and Al depends on soil pH. In carbonate-rich alkaline soil, phosphate is sorbed by calcite, but at higher concentrations Ca phosphate may precipitate. Phosphorus adsorption on organic matter occurs in association with the metal cations Fe^{2+}, Al^{3+} and Ca^{2+}. Low P_2O_5 content in subsoil (<0.07%) occur only in eastern Finland, central Sweden, the glacial drift area from Denmark to Poland, eastern Hungary, parts of Greece, north-central and south-west France, central Portugal, and most of eastern Spain. The highest P_2O_5 content in subsoil are scattered over Europe, apparently without direct correlation to regional geology; the individual meaning of these point anomalies should be investigated locally. In north-west France, phosphorus is partly inherited from Cretaceous stratabound phosphorite mineralisation, but an influx by fertiliser cannot be excluded (Cd correlation) in that area of intensive farming; the latter explanation can be proposed for P_2O_5 enrichment in topsoil of Brittany. Other high P_2O_5 areas (>0.14%) include southern Italy, the Massif Central, north-west Spain (crystalline basement of the Iberian Massif), south-central Spain (perphosphoric granite in Sierra Morena and Extremadura), Croatia and adjacent areas, western Hungary, Austria, south-western Norway, northern Sweden and the lower-Palaeozoic phosphorite basin of northern Estonia. In Greece, two subsoil P_2O_5 point anomalies are in terra rossa soil, and in the region there is known low grade phosphate mineralization (Salminen et al., 2005).

Phosphorus is found in soil in two forms: organic and mineral. The main inorganic forms of phosphorus are phosphate ions solved in water $H_2PO_4^-$ and HPO_4^{2-}. In the soil solution of pH 4.5-7.0, phosphorus occurs

mainly as $H_2PO_4^-$ ions, which are directly absorbed by roots, and in alkaline soils as HPO_4^{2-}. These ions react readily with iron, aluminum, and manganese compounds in acid soils and with calcium compounds in neutral and alkaline soils, forming compounds which plants cannot assimilate. Due to the adsorption on the surface of the solid phase of soil and formation of insoluble phosphate precipitates, they become inaccessible to plants. About 15-80% of phosphorus in soil is found in organic compounds (nucleic acids, phospholipids, phytate) from plant residues. Phosphorus resources in soil are scarce and its total concentration ranges between 50 and 3 000 mg of phosphorus/kg (or 275 – 16 500 mg/kg expressed as pyrophosphate $P_2O_7^{4-}$). Phosphorus compounds in soil display great diversity both in terms of chemical forms and the strength of bonding with the solid phase of soil. One of the unique characteristics of phosphorus is its immobility in soil (Bezak-Mazur, 2013; Schulte and Kelling, 1996).

EU consumption of phosphorus (in the form of manufactured fertilisers) in 2009 averaged 6 kg per hectare in the EU, ranging from 2 kg per hectare in Romania to 10 kg per hectare in Poland. Between 2000 and 2008 the consumption of phosphorus-based fertilisers increased at a relatively rapid pace in Poland (5.7 % per annum) and Hungary (4.2 %). Only two other EU Member States (and Switzerland) reported growth in the quantity of phosphorous-based fertilisers that were used during the period from 2000 to 2008; while there was no change in the consumption of phosphorus-based fertilisers in Austria. In contrast, consumption of phosphorous- based fertilisers fell by between 7.4 % and 10.2 % per annum in Ireland, the Benelux countries and Portugal Based on historical data, the gross phosphorus balance for the EU-27 was assessed for the period 2005 to 2008, averaging 1.8 kg of phosphorus per hectare of agricultural land; Malta, Cyprus and several countries in north western Europe having the highest surpluses, while a deficit was recorded in eight of the Member States. Comparing the average phosphorus balance for the period from 2000 to 2004 with that for 2005 to 2008, the biggest reductions in the phosphorus balance were generally recorded among those Member States that reported some of the highest phosphorous surpluses; in particular, Belgium, Slovenia and the Netherlands. On the other hand, there were only two countries that reported an increase in their phosphorus surplus over the period under consideration – Poland and Norway (Figure 8.1-1, Table 8.1-1). (Eurostat, 2019).

Based on available statistic data for 2009, the predicted concentration of phosphorus compound in agricultural land was assessed as 8.00 mg/kg soil and its effect on soil phosphorus content is negligible as the P-compounds level in natural rock is above 100 mg/kg.

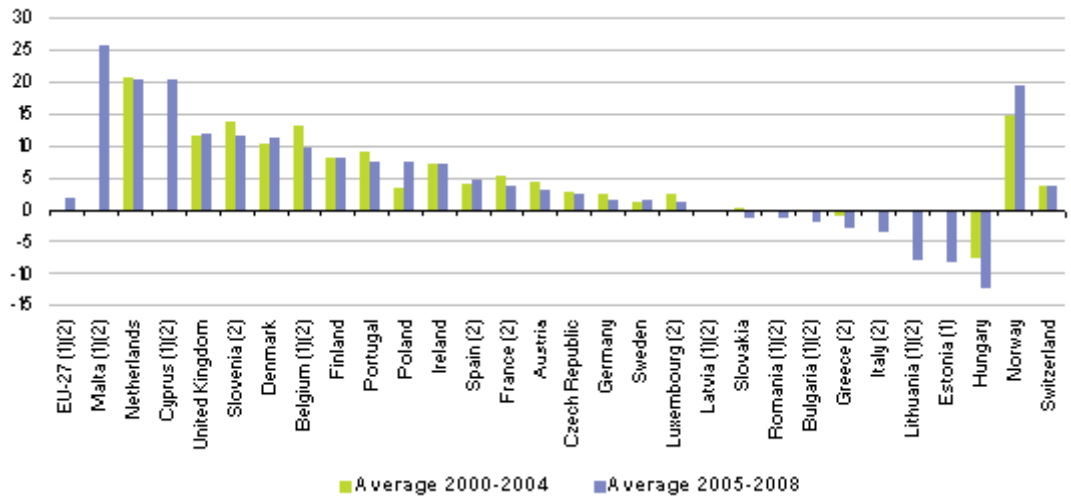

Figure 8.1-1. Gross phosphorus balance, 2000-2004 and 2005 2008 (kg phosphorus per hectare of agricultural land). (source: Eurostat, online data code: aei_pr_gnb)

Table 8.1-1. Consumption of phosphorus fertilizers in European Countries.

GEO/TIME	2009	2010	2011	2012	2013	2014	2015	2016	2017
European Union – 28 countries	1 001 392	1 189 837	1 273 347	1 226 894	1 321 325	1 311 967	1 285 614	1 308 709	1 342 473
Belgium	4 600	5 600	4 493	4 472	4 682	4 750	4 815	4 876	4 876
Bulgaria	13 387	17 043	12 902	20 798	11 656	28 144	27 573	36 050	29 562
Czech Republic	7 585	13 654	17 304	18 713	18 201	20 070	21 221	20 716	24 159
Denmark	11 000	10 000	10 000	12 800	12 300	14 000	13 800	13 800	20 800
Germany	76 122	102 675	125 025	107 880	124 073	123 999	131 503	125 643	100 894
Estonia	2 471	2 671	2 680	2 955	3 129	3 775	3 522	3 444	4 063
Ireland	20 231	28 235	28 107	27 421	36 986	35 584	36 551	37 074	41 893
Greece	24 002	30 073	25 048	21 734	25 896	24 024	21 962	22 515	28 172
Spain	115 360	147 495	158 350	164 427	189 014	174 028	179 784	181 186	190 414
France	129 142	177 025	218 428	189 633	217 184	206 798	187 054	191 677	187 931
Croatia	8 790	15 763	14 028	14 330	12 518	16 875	12 899	5 781	14 891
Italy	229 743	229 716	229 700	229 735	224 632	228 455	226 757	228 226	229 657
Cyprus	2 245	2 286	1 207	2 143	1 945	1 728	2 122	2 349	2 349
Latvia	5 831	6 840	7 640	8 648	10 670	10 204	10 633	11 111	11 300
Lithuania	14 000	15 000	16 000	17 000	18 165	19 419	19 799	22 217	23 473
Luxembourg	590	515	516	517	515	515	516	491	510
Hungary	19 232	19 976	22 113	25 735	35 708	34 365	35 063	38 474	48 030
Malta	3	31	57	28	31	28	38	56	56
Netherlands	4 043	12 513	6 081	4 611	3 984	5 869	3 736	5 211	4 674
Austria	7 256	12 527	9 947	12 301	14 234	14 110	13 058	15 451	11 789
Poland	163 852	154 183	178 318	161 883	168 295	148 917	132 544	142 281	149 950
Portugal	11 538	18 090	12 908	14 477	17 289	18 456	20 159	21 458	22 479
Romania	43 900	53 849	55 123	49 353	49 697	51 772	57 921	55 097	63 253
Slovenia	3 342	4 323	3 935	3 882	3 886	3 991	4 120	4 000	3 988
Slovakia	7 936	7 041	8 569	8 369	8 959	9 918	9 426	10 608	10 133
Finland	10 784	12 599	11 046	10 600	11 184	11 845	10 983	9 828	12 252
Sweden	8 100	9 800	10 300	10 400	11 800	12 100	12 500	13 100	14 500
United Kingdom	56 307	80 314	83 522	82 050	84 692	88 228	85 555	85 989	86 425

Norway	8 443	7 818	8 757	8 350	8 455	8 405	9 276	9 097	8 683
Switzerland	3 886	4 672	4 585	4 803	4 323	4 192	4 235	4 279	4 279

source: http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do

or

https://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=aei_fm_usefert&lang=en and choose Phosphorus

In phosphorus fertilizers, about half of phosphorus has the form of orthophosphate and the remaining phosphorus is condensed mainly as pyrophosphate. What decides about pyrophosphate being an effective source of phosphorus in a fertilizer is the rate of its hydrolysis to the orthophosphate form, which is caused almost solely by catalysis via pyrophosphatase with the presence of divalent metal ions. The hydrolysis depends on many factors such as biological activity, water content, pH, temperature. In warm wet soils, polyphosphate ions react with soil moisture to form orthophosphates relatively rapidly (1–2 weeks), whereas in cool and dry conditions, hydrolysis might proceed slower. Since practically all soluble phosphorus from fertilizer or manure is converted in the soil to water-insoluble phosphorus within a few hours after application, the use of polyphosphate fertilizers is more effective. Pyrophosphates are water-soluble and they are not considered to be as efficient as orthophosphates in terms of plant nutrition. It is well known that pyrophosphates are a relatively ineffective source of phosphorus for plants prior to hydrolysis to the orthophosphate form. Generally, the effectiveness of pyrophosphates as a source of phosphorus for plants depends on their reactions with the soil constituents and the distribution of phosphorus between ortho- and pyro-phosphates at different times during the growing season (Ahmad and Kelso, 2001).

This stems from the fact that polyphosphate compounds are less reactive in soil compared to orthophosphates and thus less prone to precipitation, which might increase availability of phosphorus in soil and its uptake by plants. Moreover, it is claimed that polyphosphates are superior to orthophosphates because they have an ability to chelate and combine with certain micronutrients (e.g. Zn) and hold them in an available form. The average use of phosphorus fertilizers in Poland in the years 2011/2012 was 24.8 kg P_2O_5/ha of arable land (Dmochowska, 2013).

In accordance with the document of the United States Environmental Protection Agency (1993), no unfavourable ecological and environmental effects of using iron salts as plant protection products have been identified. It is not expected that iron salts present in plant protection products or fertilizers will affect in any significant way the fate of compounds naturally occurring in the environment. As a result of using iron salt, ferric oxides and hydroxides are formed, which are in no way different from those naturally occurring in soil and which are responsible for its brown and red colour.

Both iron and phosphorus are natural components of soil and key nutrients for plants and animals. The amount of ferric pyrophosphate added as a result of application compliant with GAP will be negligible compared to the amount naturally occurring in the environment. As for toxicity to man and ecotoxicity, there are no specific concerns about the fate and behavior of ferric pyrophosphate in soil after application compliant with GAP, thus no studies on fate and behavior in soil were conducted.

RMS comments and conclusion

Information on iron ions and phosphates, including pyrophosphates, in soil were submitted by the Applicant and evaluated. The literature review concerning the amounts of iron and phosphorus compounds was analysed and accepted as a supportive data. These data were taken from literature review not from relevant studies performed for active substance. The studies concerning the ferric pyrophosphate direct effect on soil are not available.

The submitted data in general refer to information on iron and phosphorus originate and their background level in soil. These data can be used for comparison analysis concerning natural and anthropogenic use of both ions (fertilisers and other chemicals). It is worth noting that phosphorus fertilizers use differs in EU Member States.

B.8.1.1 Route of degradation in soil

Based on the information and arguments presented in point B.8.1, further data on route of degradation of ferric pyrophosphate in soil are not required.

B.8.1.1.1 Aerobic degradation

Based on the information and arguments presented in point B.8.1, further data on route of degradation of ferric pyrophosphate in soil are not required.

B.8.1.1.2 Anaerobic degradation

Based on the information and arguments presented in point B.8.1, further data on route of degradation of ferric pyrophosphate in soil are not required.

B.8.1.1.3 Soil photolysis

Based on the information and arguments presented in point B.8.1, further data on route of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2 Rate of Degradation in Soil

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2.1 Laboratory studies

B.8.1.2.1.1 Aerobic degradation of the active substance

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2.1.3 Anaerobic degradation of the active substance

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2.2 Field Studies

B.8.1.2.2.1 Soil dissipation studies

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.2.2.2 Soil accumulation studies

Based on the information and arguments presented in point B.8.1, further data on rate of degradation of ferric pyrophosphate in soil are not required.

B.8.1.3 Absorption and desorption in soil

Based on the information and arguments presented in point B.8.1, further data on adsorption and desorption of ferric pyrophosphate in soil are not required.

B.8.1.3.1 Adsorption and desorption

B.8.1.3.1.1 Adsorption and desorption of the active substance

Based on the information and arguments presented in point B.8.1, further data on adsorption and desorption of ferric pyrophosphate in soil are not required.

B.8.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

Based on the information and arguments presented in point B.8.1, further data on adsorption and desorption of ferric pyrophosphate in soil are not required.

B.8.1.3.2 Aged sorption

Based on the information and arguments presented in point B.8.1, further data on aged sorption of ferric pyrophosphate in soil are not required.

B.8.1.4 Mobility in soil

Based on the information and arguments presented in point B.8.1, further data on mobility of ferric pyrophosphate in soil are not required.

B.8.1.4.1 Column leaching studies

B.8.1.4.1.1 Column leaching of the active substance

Based on the information and arguments presented in point B.8.1, further data on mobility of ferric pyrophosphate in soil are not required.

B.8.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

Based on the information and arguments presented in point B.8.1, further data on mobility of ferric pyrophosphate in soil are not required.

B.8.1.4.2 Lysimeter studies

Based on the information and arguments presented in point B.8.1, further data on mobility of ferric pyrophosphate in soil are not required.

B.8.1.4.3 Field leaching studies

Based on the information and arguments presented in point B.8.1, further data on mobility of ferric pyrophosphate in soil are not required.

B.8.2 Fate and Behaviour in Water and Sediment

Iron in stream sediment

The median total iron content in stream sediment, expressed as Fe_2O_3 is 3,58 % with a range varying from 0.11 to 18.3%. Low Fe values in stream sediment (<2.24% Fe_2O_3) occur mainly in the glacial drift area from Poland to the Netherlands, in Latvia, Estonia, north-western and south-western France, the Jura Mountains, parts of eastern Spain, and central Austria.

High Fe_2O_3 values in stream sediment (>5.15%) are found throughout southern and northern Finland (iron ores), northern and central Sweden, northern Norway (Caledonian layered mafic intrusions such as Sulitjelma), and the Caledonides of Norway generally. The North-Atlantic Tertiary volcanic province shows high Fe values in western Scotland (central complexes of Skye, Mull, Rhum and Ardnamurchan) and in northern Ireland (Antrim plateau basalt). In north-western Ireland a base-metal mineralisation causes an anomaly in Fe, Pb, Cu, Mn, Sb, As, Ge, Co, Ba. Most of Britain shows high Fe values, which may be caused by secondary precipitation in stream sediment. In central and southern Europe, in contrast, Fe anomalies in stream sediment are scarce, limited to southern Portugal and adjacent Spain (Iberian Pyrite Belt and Ossa Morena metamorphic zone with Fe mining), north-western Spain (Ordovician quartzite with Fe-oxides and Fe-oolithic mineralisation), the Central Pyrenees (supergene Fe-oxide precipitation, with Fe coming from Silurian black shale with pyrite), the Roman Alkaline Province in Italy, point anomalies on basaltic rocks of the Canary Islands, the Etna volcanic area in Sicily, Roccamonfina in Campania, and eastern Greece

(ophiolite, Fe-Ni deposits, bauxite and polymetallic mineralisation). In addition, scattered point anomalies throughout Europe could be caused by local geological substrate or by oxidising precipitation conditions in stream sediment (Salminen et al., 2005).

Phosphorus in stream sediment

The median P_2O_5 content in stream sediment is 0.13%, with a range of values from <0.01 to 2.47%.

Low P_2O_5 areas in stream sediment (<0.09%) include eastern Finland, central and eastern Norway, Estonia, parts of Poland, northern Denmark, Aquitaine, Normandy and the Rhône valley in France, northern Italy (a belt from Tuscany to central Austria) and Albania.

High values of total P_2O_5 in stream sediment (>0.21%) are confined to some well-defined areas, the largest extending from Denmark over eastern Germany and adjacent parts of south-west Poland to the Czech Republic, mostly attributed to agricultural activities (although in the southern Czech Republic a local durbachite ultramafic rock is enriched in phosphorus). Phosphate is also high in central and eastern England; small areas in eastern Poland and southern Lithuania (caused by agricultural pollution, i.e., use of fertilizer and pig or cow manure in flat sandy glaciofluvial terrain with high groundwater level); and Apulia in southern Italy. Fertiliser use is probably responsible for most of the high values listed above. Elsewhere the link with fertilisers is not clear, and natural causes could account for the high values: the Massif Central in France, northern Portugal (igneous rocks), the Sierra de Gredos in central Spain (granitic rocks), northern Ireland and northern Scotland, northern Greece (intrusive rocks), a point anomaly near Verona (Italy) possibly related to basaltic rocks, a point anomaly in southern Hungary, a larger area in south-western Norway (igneous rocks) and a few more scattered points in Norway; a large area in southern Sweden and more areas throughout central and northern Sweden. In France, some similarity exists between the distribution of P, Mn and Fe, an association known to be related to the palaeoshoreline of the upper Cretaceous sea (Cenomanian), (Salminen et al., 2005).

The active substance is an inorganic salt poorly soluble in water (40 µg/l). Iron salts, iron and phosphorus naturally occur both in aquatic and terrestrial ecosystems. Inorganic iron and phosphorus ions do not degrade and comprise a natural fertilizer for algae and plants. In moderate and high temperatures, increased level of phosphorus in surface waters causes eutrophication i.e. explosive growth of algae accompanied with a decrease in dissolved oxygen.

RMS comments and conclusion

Information on behavior of ferric pyrophosphate in water and sediment is sufficient as a supportive data. These data were taken from literature review not from relevant studies performed for active substance. The studies concerning the ferric pyrophosphate direct effect on water and sediment are not available.

Ferric pyrophosphate is practically insoluble in water, so the submitted information concerns the sediment. The amounts of iron and phosphate ions which will be present in aquatic compartment from the representative uses are limited compared to the iron and phosphate ions naturally present in water and sediment.

B.8.2.1 Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.1.1 Hydrolytic degradation

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.1.2 Direct photochemical degradation

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.1.3 Indirect photochemical degradation

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.2 Route and rate of biological degradation in aquatic systems

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.2.1 "Ready biodegradability"

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.2.2 Aerobic mineralisation in surface water

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.2.3 Water/sediment studies

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.2.4 Irradiated water/sediment study

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.2.3 Degradation in the Saturated Zone

Based on the information and arguments presented in point B.8.2, further data on fate and behavior of ferric pyrophosphate in water are not required.

B.8.3 Fate and Behaviour in Air

Ferric pyrophosphate is a non-volatile salt and so no further data is required regarding its fate and behavior in air.

RMS comments and conclusion

Information on behavior of Ferric pyrophosphate in air is sufficient.

B.8.3.1 Route and rate of degradation in air

Ferric pyrophosphate is a non-volatile salt and so no further data are required regarding its fate and behavior in air.

B.8.3.2 Transport via air

Ferric pyrophosphate is a non-volatile salt and so no further data are required regarding its fate and behavior in air.

B.8.3.3 Local and global effects

Ferric pyrophosphate is a non-volatile salt and so no further data are required regarding its fate and behavior in air.

B.8.4 Definition of the Residue

As presented in chapters B.8.1 – 8.3 on fate and behavior of ferric pyrophosphate in the environment, the substance is a stable non-volatile salt, virtually insoluble in water. There are no decomposition products other than iron and phosphates. Both iron and phosphorus occur naturally in the environment, and the amount of ferric pyrophosphate added to soil as a result of application compliant with GAP will be negligible compared to the natural content of iron and phosphorus in soil. In the following environmental compartments, the residues of ferric pyrophosphate were taken into consideration:

- Soil,
- Surface water,
- Sediment,
- Ground water.

RMS comments and conclusion

The residues are reported in relevant sections.

B.8.4.1 Definition of the residue for risk assessment

Based on the information presented in point B.8.4, it is not necessary to formulate a definition of residues for risk assessment purposes.

B.8.4.2 Definition of the residue for monitoring

Based on the information presented in point B.8.4, it is not necessary to formulate a definition of residues for monitoring purposes.

B.8.5 Monitoring Data

There exists no data on monitoring that could be directly related to the use of ferric pyrophosphate as a molluscicide.

B.8.6 References relied on

Reference number	Author(s)	Year	Title Source (where different from company) Company, Report No GLP or GEP status (where relevant) Published or not	Data Protection Claimed Y / N	Owner
B.8.1 also B.6 B.7.2	Anonymous	1993	*United States Environmental Protection Agency; Reregistration eligibility Document (RED): Iron Salts US EPA* nGLP / Published	N	Public
B.8.1 also B.6 B.7.2	Draggan S. et al.	2011	*Mineral Information Institute: Iron. Publication online http://www.eoearth.org/view/article/ 51cbee407896bb431f696707* nGLP / Published	N	Public
B.8.1 also B.6 B.7.2	Schulte E.E.	1992	*Understanding Plant Nutrients: Soil and Applied Iron* nGLP / Published	N	Public
B.8.1 also B.7.2	Chen Y., Shenker M.	2004	*Agronomic approaches for increasing iron availability to food crops. W: Impacts of Agriculture on Human Health and Nutrition. pod red. Welch R.M., Cakmak I., Encyclopedia of Life Support Systems (EOLSS), UNESCO, Publication online: http://www.eolss.net, 2004* nGLP / Published	N	Public
B.8.1 also B.7.2	Anonymous	2003	*United States Environmental Protection Agency, Ecological Soil Screening Level for Iron* *OSWER Directive 9285.7-69* nGLP / Published	N	Public
B.8.1 also B.7.2	Schulte E.E., Kelling K.A.	1996	*Understanding Plant Nutrients: Soil and Applied Phosphorus;* nGLP / Published	N	Public
B.8.1 also B.6 B.7.2 B.8.2	Bezak-Mazur E., Stoińska R.	2013	*The importance of phosphorus in the environment – review article. Archives of Waste Management and Environmental Protection 15, 33-42* nGLP / Published	N	Public
B.8.1 also B.6 B.7.2 B.8.2	Fruzinska R.	2011	*Accumulation of iron in the soil – plant system in a metal industry area. Civil and Environmental Engineering Reports No 7, 2011* nGLP / Published	N	Public
B.8.1	Liu G., Hanlon E., Li Y.	2012	*Understanding and Applying Chelated Fertilizers Effectively Based on Soil pH. HS1208. University of Florida Institute of*	N	Public

			Food and Agricultural Sciences; Publication online: http://edis.ifas.ufl.edu/pdffiles/HS/HS120800.pdf nGLP / Published		
B.8.1 B.7.2	Chohura P.	2005	*Nawożenie roślin ogrodniczych żelazem (Role of iron and plant requirement) Hasło Ogrodnicze; Publication online: http://www.ho.haslo.pl/article.php?id=2213&rok=2005&numer=05* nGLP / Published	N	Public
B.8.1	Ahmad F., Kelso W.I.	2001	*Pyrophosphate as a source of phosphorus: hydrolysis under different conditions. Journal of Research Science 12,pp. 130-139* nGLP / Published	N	Public
B.8.1	Salminen R.et al	2005	*Geochemical Atlas of Europe, Part 1 Background Information, Methodology and Maps http://weppi.gtk.fi/publ/foregsatlas/maps_table.php* nGLP / Published	N	Public
B.8.1	Dmochowska H., ed	2013	*Rocznik Statystyczny Rolnictwa, str. 137, Główny Urząd Statystyczny, Warszawa (Statistical Yearbook of Agriculture, p.137, Central Statistical Office), Warsaw,* nGLP / Published	N	Public
B.8.1	-	2019	*Eurostat Statistic Explained. Agri-Environmental Indicator- Mineral Fertiser Consumption. https://ec.europa.eu/eurostat/statistics-explained/index.php/Agri-environmental_indicator_-_mineral_fertiliser_consumption* nGLP / Published	N	Public
B.8.1	-	2015	*Conclusion on the peer review of the pesticide risk assessment of the active substance ferric phosphate EFSA Journal 2015;13(1):3973* nGLP / Published	N	Public