

# **Draft Assessment Report**

## **Evaluation of Active Substances**

Plant Protection Products

Prepared according to **Regulation (EC) 1107/2009**  
as it applies in Great Britain

### **Elemental iron**

### **Volume 3 – B.8 (AS)**

Great Britain

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## Version History

When	What
November 2021	Initial DAR
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## B.8. ENVIRONMENTAL FATE AND BEHAVIOUR

This Draft Assessment Report (DAR) concerns the new active substance elemental iron, submitted for approval in the UK. Iron is a naturally occurring metal, ubiquitously found in the environment. Iron is the fourth most abundant element and the second most abundant metal, accounting for 5.1% (by weight) of the Earth's crust. Elemental iron ( $\text{Fe}^0$ ) is rarely found in nature, as the iron ions  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  readily combine with oxygen- and sulphur-containing compounds to form oxides, hydroxides, carbonates, and sulphides (WHO, 2003). Iron compounds are released through the weathering of soil and rocks and are most commonly found in the form of its oxides. These naturally occur in terrestrial and aquatic ecosystems.

The formulated product, '*Final Bite*', is a molluscicide intended to be applied in granular form at a rate of 6x 80 g/ha per year. Details of the proposed uses and the exposure assessments for each environmental compartment are presented in the volume 3 CP Part B.8.

Due to the nature of this active substance, a case has been presented in order to waive several data requirements. This document will explore the naturally occurring background levels of iron and describe its environmental behaviour and processes.

Table 3CA B.8-1 Physicochemical properties of elemental iron

Property	Active substance*
Molar mass [g/mol]	55.85
Molecular formula/ structure	Fe (element)
Solubility in water (at 20°C) [mg/L]	Elemental iron is insoluble in water.
Vapour pressure (at 20°C) [Pa]	Iron is an inorganic solid with negligible volatility under ambient conditions.
log Pow (at 20°C) (n-Octanol/water partition coefficient)	Not relevant since iron is not soluble in water or organic solvents.
Henry's Law Constant (at 20°C) [Pa m <sup>3</sup> /mol]	A Henry's law constant is not applicable since iron is not volatile and is insoluble in water.

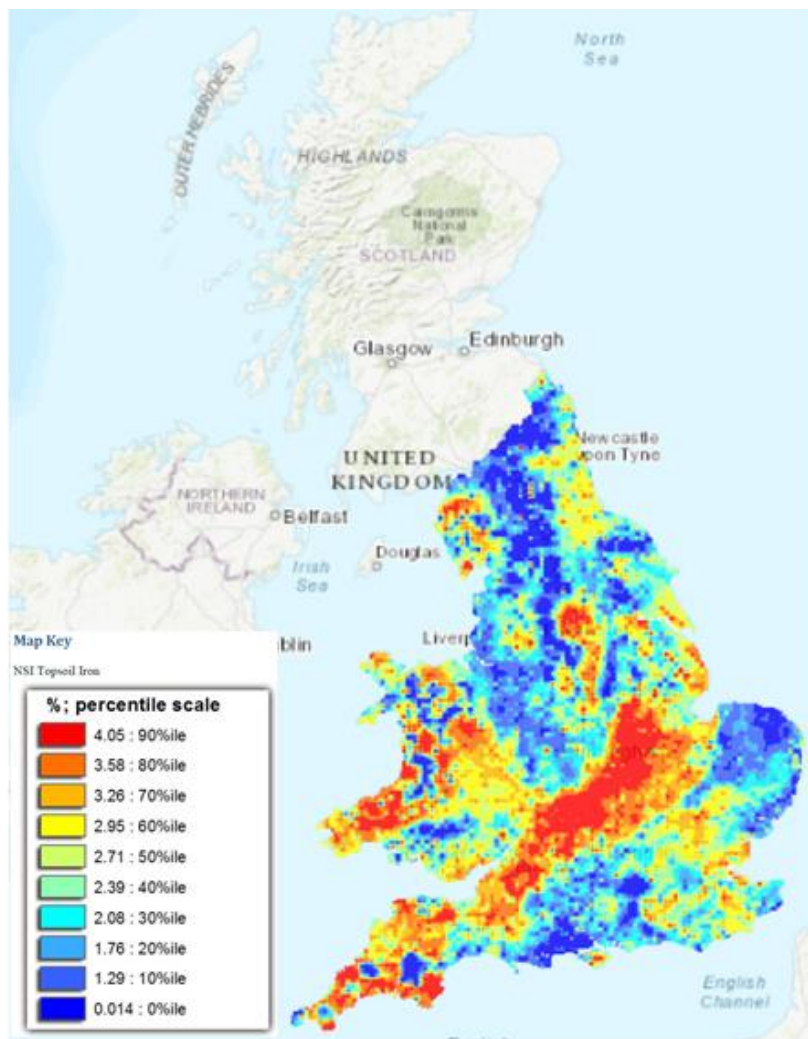
\* These physicochemical properties are specifically for the elemental form of iron,  $\text{Fe}^0$ . Upon contact with oxygen and water in the environment,  $\text{Fe}^0$  may undergo redox reactions to form ions and complexes, which may have different physicochemical properties. Refer to document DAR Volume 3CP Section B.8 for the physicochemical properties used in the environmental exposure modelling.

### B.8.1. FATE AND BEHAVIOUR IN SOIL

#### B.8.1.1. Route and rate of degradation in soil

##### *Naturally occurring background levels*

Iron is present in all soil environments as a result of the weathering of rocks and minerals. It is a key structural element in layer silicate clays, iron and aluminium oxide clays and amorphous clays which form major components of soils worldwide (Brady, 1990). The total iron content of soils varies between 0.2 to 5 % (Scheffer & Schachtschabel, 1992 and the ferric phosphate DAR), influenced by a combination of underlying geology, weathering, land use and industrial activities. Data for England and Wales indicates that higher concentrations of iron (> 3.5 %) can be found in a band from the South-West to Lincolnshire, with lower concentrations (<1 %) associated with the upland areas of Northern England and Wales, the South-West peninsula, and sandy soils associated with heathland and East Anglia (Rawlins *et al.*, 2012).

Figure 3CA B.8.1.1-1 Topsoil iron concentrations in England and Wales (UK Soil Observatory, no date.)

The process for data collection and analysis of soil samples collected for the National Soil Inventory database is described in appendix 3CA B.8.7.

#### *Iron speciation in the environment*

Iron rarely remains in the form of elemental iron ( $\text{Fe}^0$ ) in the environment and readily undergoes reactions to reflect changes in oxygen concentration and pH conditions (Vance, 1994). Iron will exist in one of two oxidation states: reduced ferrous iron ( $\text{Fe}^{2+}$ ) or oxidised ferric iron ( $\text{Fe}^{3+}$ ), which will be present either as solids in minerals or as ions dissolved in water (Pérez-Guzmán *et al.*, 2010).  $\text{Fe}^{3+}$  is the most common form as iron is readily exposed to oxygen and water in the environment (reaction described below). Under normal environmental conditions  $\text{Fe}^{3+}$ , commonly referred to as rust, is insoluble and appears powdery and red (Pérez-Guzmán *et al.*, 2010). Table B.8.1.1-1 describes the common iron-containing minerals.

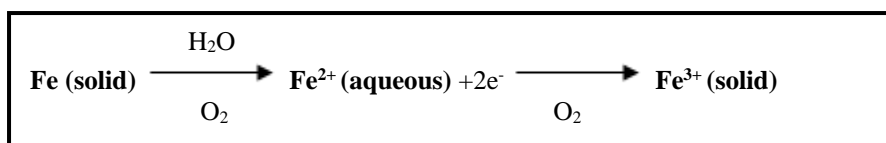
Figure 3CA B.8.1.1-2 Common redox reactions of iron in the environment in the presence of oxygen and water

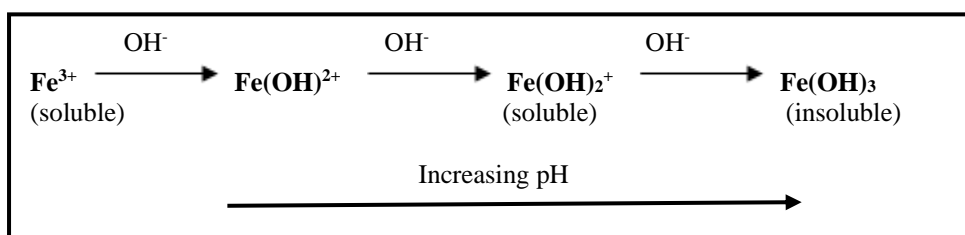
Table 3CA B.8.1.1-1 Common iron-containing minerals found on Earth

Oxides		Oxy-hydroxides		Hydroxides	
Mineral	Formula	Mineral	Formula	Mineral	Formula
Hematite	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Akaganéite	$\beta$ -FeOOH	Bernalite	Fe(OH) <sub>3</sub>
Maghemite	$\beta$ -Fe <sub>2</sub> O <sub>3</sub>	Feroxyhite	$\delta'$ -FeOOH		Fe(OH) <sub>2</sub>
	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Ferrihydrite	Fe <sub>5</sub> HO <sub>8</sub> + 4H <sub>2</sub> O	Green rust*	-
	$\epsilon$ -Fe <sub>2</sub> O <sub>3</sub>	Goethite	$\alpha$ -FeOOH		
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	Lepidocrocite	$\gamma$ -FeOOH		
Wüstite	FeO	Schwertmannite	$\delta$ -FeOOH		

\* In general, green rusts have the formula Fe<sup>3+</sup><sub>x</sub> Fe<sup>2+</sup><sub>y</sub> (OH)<sub>3x+2y-z</sub> (A<sup>-</sup>); where A<sup>-</sup> = Cl<sup>-</sup> or ½ SO<sub>4</sub><sup>2-</sup> (Pérez-Guzmán *et al.*, 2010)

### Effects of pH and oxygen

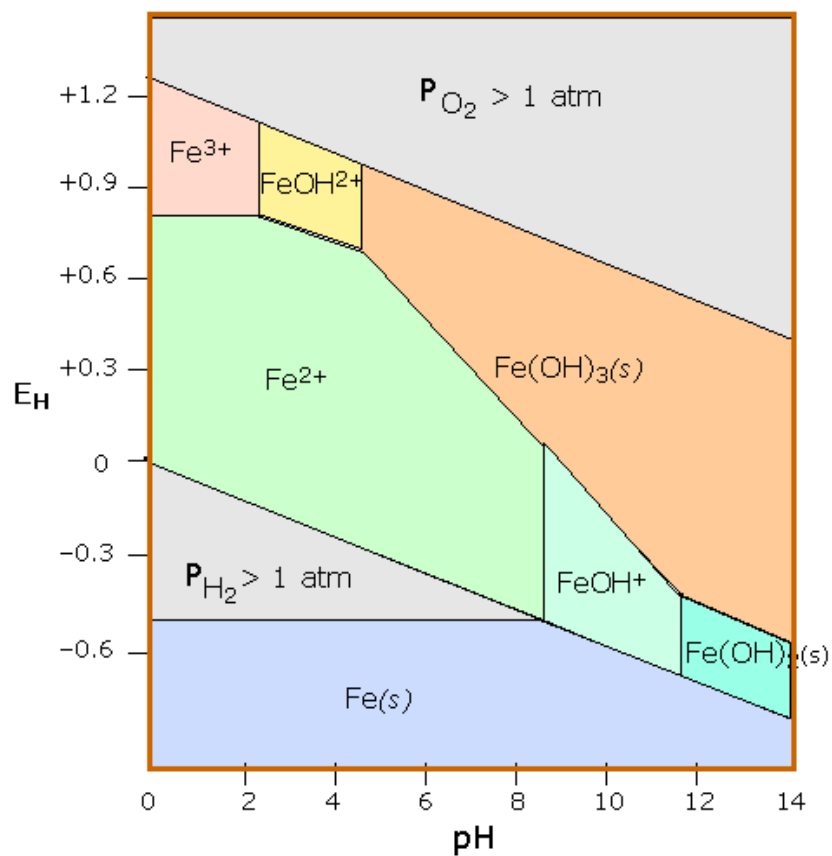
Fe<sup>3+</sup> ions are insoluble at and around neutral pH, however they can become soluble under strongly acidic or alkaline conditions (Pérez-Guzmán *et al.*, 2010). The reduced form Fe<sup>2+</sup> is soluble over a much greater pH range (< pH 8.5) but requires a lower redox potential (Younger, 2007). The reduced Fe<sup>2+</sup> ion is only stable at neutral or alkaline pH under anaerobic conditions and will rapidly oxidise to Fe<sup>3+</sup> when exposed to oxygen in moist environments (Pérez-Guzmán *et al.*, 2010).

Figure 3CA B.8.1.1-3 Reactions of iron with water over increasing pH

(Brady, 1990)

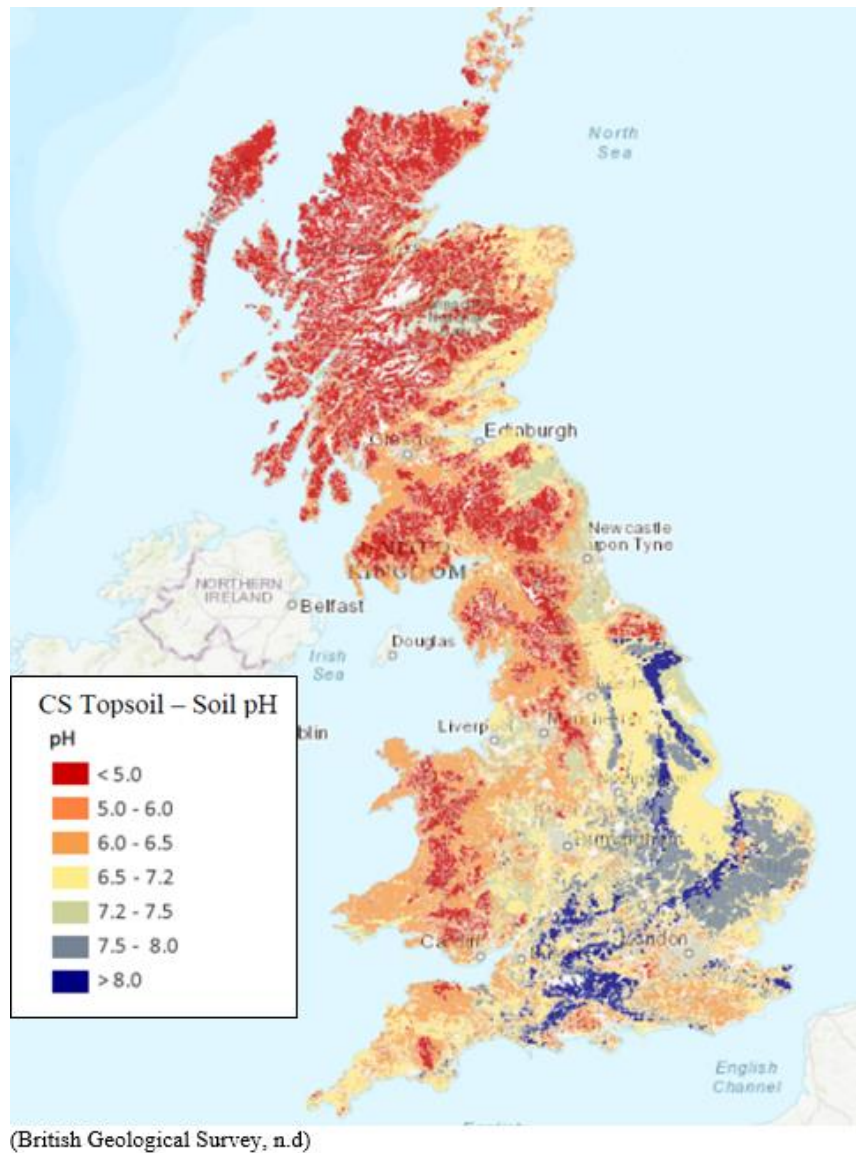
The Pourbaix diagram below shows the stability of the various iron oxidation states and compounds over a range of redox ( $E_H$ ) and pH values. It shows that elemental iron Fe<sup>0</sup> is stable over a very wide range of pH values. The oxidised form, Fe<sup>3+</sup> ions are only present as free ions in extremely acidic conditions (<pH 2), which are unlikely to occur in the natural environment. However, it shows that free Fe<sup>2+</sup> ions are present at neutral and slightly alkaline conditions, under more reducing conditions. UK topsoil pH values range from <5 to >8 (see map figure B.8.1.1-5), with more acidic soils in upland areas in Scotland, Wales, Northern England and South-West England. Under acidic soils, the redox potential does not need to be as low for free Fe<sup>2+</sup> ions to be present.

Figure 3CA B.8.1.1-4 Pourbaix diagram for iron showing the stability of the different oxidation states and iron compounds under a range of pH and redox conditions



**Pourbaix diagram for iron:** Three oxidation states of iron (0, +2 and +3) are represented on this diagram. The stability regions for the oxidized iron states are shown only within the stability region of H<sub>2</sub>O. Equilibria between species separated by vertical lines are dependent on pH only. (ChemLibre texts, 2019).

Figure 3CA B.8.1.1-5 UK topsoil pH (0-15 cm)



#### *Interactions with plants and microorganisms*

Iron is an essential micronutrient for most organisms and is involved in important cellular processes such as respiration, oxygen transport in the blood, photosynthesis, nitrogen fixation, and nitrate reduction (Pérez-Guzmán *et al.*, 2010). Microorganisms play a vital role in iron redox reactions in most environments and can oxidise or reduce iron compounds in either oxic or anoxic conditions (Weber *et al.*, 2006a). However, microbial reduction of  $\text{Fe}^{3+}$  oxides and hydroxides normally occurs in oxygen deficient, poorly drained or flooded soils.

Plants primarily use  $\text{Fe}^{2+}$  ions and use various mechanisms to reduce  $\text{Fe}^{3+}$  ions to be able to uptake iron into the roots (Vitosh *et al.*, 1994). The two tables below show the acceptable or sufficient nutrient concentration of iron required for production of several crops (Vitosh *et al.*, 1994) and (Fageria *et al.*, 1990). These show that the overall sufficiency range is approximately 11-600 mg/kg for a range of agricultural crops.



Table 3CA B.8.1.1-2 Acceptable or sufficient nutrient concentration ranges required for production of several crops

ELEMENT	CORN Ear leaf sample of initial silk	SOYBEANS Upper fully developed leaf sampled prior to initial flowering	ALFALFA Top 6 inches sampled prior to initial flowering	WHEAT Upper leaves sampled prior to initial bloom	SUGAR BEETS Center fully developed leaf sampled in midseason	VEGETABLES Top fully developed leaves	POTATOES Petioles from most recently matured leaf sampled in midseason
Percent (%)							
Nitrogen	2.76-3.50	4.26-5.50	3.76-5.50	2.59-3.00	3.01-4.50	2.50-4.00	2.50-4.00
Phosphorus	0.25-0.50	0.26-0.50	0.26-0.70	0.21-0.50	0.26-0.50	0.25-0.80	0.18-0.22
Potassium	1.71-2.50	1.71-2.50	2.01-3.50	1.51-3.00	2.01-6.00	2.00-9.00	6.00-9.00
Calcium	0.21-1.00	0.36-2.00	1.76-3.00	0.21-1.00	0.36-1.20	0.35-2.00	0.36-0.50
Magnesium	0.16-0.60	0.26-1.00	0.31-1.00	0.16-1.00	0.36-1.00	0.25-1.00	0.17-0.22
Sulfur	0.16-0.50	0.21-0.40	0.31-0.50	0.20-0.40	0.21-0.50	0.16-0.50	0.21-0.50
Parts per million (ppm)							
Manganese	20-150	21-100	31-100	16-200	21-150	30-200	30-200
Iron	21-250	51-350	31-250	11-300	51-200	50-250	30-300
Boron	4-25	21-55	31-80	6-40	26-80	30-60	15-40
Copper	6-20	10-30	11-30	6-50	11-40	8-20	7-30
Zinc	20-70	21-50	21-70	21-70	19-60	30-100	30-100
Molybdenum	0.1-2.0	1.0-5.0	1.0-5.0	0.03-5.0	.15-5.0	0.5-5.0	0.5-4.0

Table 3CA B.8.1.1-3 Iron sufficiency levels for different crops

Crop	Plant part analysed	Stage of growth	Sufficiency range (mg/kg)	References
Barley	Whole tops	Heading	50 - 150	Ward et al. 1973
Common bean	Fully developed Trifoliolate	Flowering	100 - 450	Wilcox & Fageria 1976
Corn	Ear leaf	At silk	50 - 200	Jones Júnior & Eck 1973
Cotton	Mature leaves	Early bloom	30 - 300	Sabbe et al. 1972
Peanut	Upper stem & leaves	Flowering	50 - 300	Small & Ohlrogge 1973
Rice	Whole top	Tillering	70 - 300	Fageria 1984
Sorghum	3rd leaf	At bloom below head	65 - 100	Lockman 1972
Sugar beet	Blade	Not given	60 - 140	Nagarajah & Ulrich 1966
Sugar cane	Blade	Not given	20 - 600	Schmehl & Humbert 1964
Soybean	Fully developed Trifoliolate	Prior to pod set	51 - 350	Small & Ohlrogge 1973
Wheat	Whole tops	Heading	50 - 150	Ward et al. 1973

*Iron added as a micronutrient*

Plants uptake significant quantities of iron from the soil. Iron availability is a limiting factor for plant growth and so it is often added as fertiliser. Fertilisers contain iron in the form of ferrous sulphate (~20% iron) or in a chelated form (6-12% iron). Approximate doses of fertiliser containing 6 - 7% iron, recommended in garden plant cultivation are as follows: 600 g Fe/ha as preventive measure, 3000 g Fe/ha in the case of moderate deficiency and 6000 g Fe/ha in the case of serious deficiency. These doses are significantly higher than the maximum total dose of elemental iron granules requested for this submission (480 g a.s./ha).

In conclusion no data regarding the fate and behaviour of elemental iron is required. The HSE has considered this based on the distribution and magnitude of occurrence of iron in the environment and the natural processes it undergoes, the inherent function (as an essential nutrient) in the metabolic pathway of animals and plants and the use of iron as a dietary supplement in food.

**B.8.1.1.1 Route and rate of degradation in aerobic soil**

Iron is a metal element and cannot be degraded as such. Therefore, the HSE considers that it is not necessary to perform a laboratory study assessing the aerobic route and rate of degradation in soil. The

processes of transformation that elemental iron readily undergoes in the soil environment are described in detail above in section B.8.1.1. Under aerobic conditions, iron will primarily be present as insoluble  $\text{Fe}^{3+}$  ions and insoluble oxide and hydroxide minerals. The HSE considers that the application of iron granules will not result in any transformation processes that are not already occurring in the natural environment. Furthermore, the predicted environmental concentrations in soil ( $\text{PEC}_{\text{SOIL}}$ ) based on year-on-year applications of the intended maximum rate are negligible compared to naturally occurring background levels. The  $\text{PEC}_{\text{SOIL}}$  accumulation value based on 20 consecutive years without tillage is 12.8 mg/kg which is considerably less than the range naturally observed in UK and European soils (140- 22,300 mg/kg) (see section 3CP B.8.2.)

#### **B.8.1.1.2 Route and rate of degradation in anaerobic soil**

Very acidic, poorly drained soils can have toxic quantities of iron (Brady, 1990). Under anaerobic conditions, particularly in flooded fields, iron will be present mostly as soluble  $\text{Fe}^{2+}$  ions (Fageria *et al.*, 1990). However, elemental iron granules are unlikely to be applied as a plant protection product to soils experiencing prolonged anaerobic conditions as these soils will be unsuitable for cultivation of crops. For intended uses on amenity vegetation, it is also unlikely that granules would be applied during extreme flooding events. Furthermore, the soil concentration resulting from the maximum application rate is significantly less than naturally occurring background levels in soil. Applications of elemental iron will not undergo any processes in the environment that are not already occurring to iron naturally present in the environment. Therefore, the HSE considers that it is not necessary to perform a laboratory study assessing the route and rate of anaerobic degradation in soil.

#### **B.8.1.1.3 Photolysis in soil**

The HSE cannot find reference to elemental iron or the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions undergoing transformation processes via exposure to irradiation. Applications of elemental iron will not undergo any processes in the environment that are not already occurring to iron naturally present in the environment. Therefore, it is considered acceptable to waive data requirements for photolytic degradation in soil.

#### **B.8.1.1.4 Field degradation studies**

The processes of transformation that elemental iron readily undergoes in the soil environment are described in detail above in B.8.1.1. Applications of elemental iron will not undergo any processes in the environment that are not already occurring to iron naturally present in the environment. Therefore, the HSE considers that it is not necessary to perform field dissipation studies for the active substance. Such studies would be redundant as it would not be possible to differentiate the active substance from the iron naturally present in the soil.

### **B.8.1.2. Adsorption and desorption in soil**

The processes of transformation that elemental iron readily undergoes in the soil environment are described in detail above in B.8.1.1. In typical aerobic soils (pH 5- 9), iron will be present in insoluble  $\text{Fe}^{3+}$  complexes such as oxides and hydroxides, and relatively immobile. Under prolonged anaerobic conditions, the fraction of mobile, soluble  $\text{Fe}^{2+}$  ions increases, however such conditions are unsuitable for agricultural cultivation. Applications of elemental iron granules will not undergo any processes in the environment that are not already occurring to iron naturally present in the environment. Therefore, the HSE considers that it is not necessary to perform adsorption studies for the active substance.

#### **B.8.1.3. Mobility in soil**

See B.8.1. and B.8.1.2. The HSE considers it is not necessary to perform mobility studies for the active substance.

## **B.8.2. FATE AND BEHAVIOUR IN WATER AND SEDIMENT**

Iron is found in natural aquatic systems, particularly in the sediment compartment. The speciation of iron and its bioavailability to aquatic organisms will depend on the redox conditions. Iron will be present as insoluble  $\text{Fe}^{3+}$  oxide and hydroxide complexes in most oxygenated waters at circumneutral pH conditions (Xing & Liu, 2011). This will precipitate to the sediment layer. It is well documented that iron undergoes reduction in sediment as a function of depth due to decreasing oxygen levels. For example, one study that assessed core samples of lake sediment found that in the top 1 cm layer, all iron was present in the oxidised  $\text{Fe}^{3+}$  form, but  $\text{Fe}^{2+}$  ions were dominant below 2 cm, with the reduced form accounting for 80% at 8 cm depth (Kappler *et al.*, 2004). Furthermore, the study found that the amount of total extractable iron increased with depth from 32 Wmol in the surface layer to 68 Wmol at 20 cm, due to a higher density and lower porewater content of the sediment at greater depths. This indicates that iron naturally accumulates in sediments.

Soluble  $\text{Fe}^{2+}$  ions are the most bioavailable form that can pass through cellular membrane or be uptaken by aquatic plants (Xing & Liu, 2011). Macrophytes can also produce siderophores (organic chelating molecules that find and solubilise  $\text{Fe}^{3+}$  ions from the ambient environment) in order to uptake  $\text{Fe}^{3+}$  ions (Xing & Liu, 2011). Microbial oxidation and reduction of iron in aquatic environments plays an important role in biogeochemical cycling and is well documented (Weber *et al.*, 2006b; Lovley & Phillips, 1986; King & Garey, 1999).

The maximum application rate of elemental iron granules is less than the naturally occurring background levels in soil. Any iron entering the aquatic environment as a result of drainflow or runoff will be negligible compared to that resulting from natural processes. The HSE considers it acceptable that no environmental fate studies have been submitted for the active substance to assess the behaviour in water and sediment.

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

#### **B.8.2.1.1 Hydrolytic degradation**

The redox reactions of iron with oxygen and water are described under section 3CA B.8.1. and B.8.2. Elemental iron applied as granules will not undergo any reactions that are not already occurring to iron naturally present in the aquatic environment. The HSE considers it acceptable to waive data requirements for the hydrolytic degradation of iron.

#### **B.8.2.1.2. Aqueous photolysis**

Elemental iron applied as granules will not undergo any reactions that are not already occurring to iron naturally present in the aquatic environment. The HSE considers it acceptable to waive data requirements for the aqueous photolysis of iron.

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

#### **B.8.2.2.1 Ready biodegradability**

Elemental iron applied as granules will not undergo any reactions that are not already occurring to iron naturally present in the aquatic environment. The HSE considers it acceptable to waive data requirements for the ready biodegradability of iron.

#### **B.8.2.2.2 Aerobic mineralisation**

Elemental iron applied as granules will not undergo any reactions that are not already occurring to iron naturally present in the aquatic environment. The HSE considers it acceptable to waive data requirements for the aerobic mineralisation of iron.

#### **B.8.2.2.3 Water sedimentation**

The environmental behaviour and speciation of iron in freshwater sediment systems is described under 3CA B.8.2. Elemental iron applied as granules will not undergo any reactions that are not already occurring to iron naturally present in the aquatic environment. The HSE considers it acceptable to waive data requirements for the behaviour of iron in water sediment systems.

### B.8.2.3. Degradation in the saturated zone

#### B.8.2.3.1 Water treatment processes

Article 4.3(b) of Regulation 1107/2009 states that “*active substances shall not have harmful effects on human health... taking account of substances resulting from water treatment*”. As iron and its various complexes naturally occur in surface water and groundwater, water treatment plants already use several methods to control the levels of iron in drinking water. Coagulation and flocculation; rapid gravity sand filters; aeration and the control of pH are all effective water treatment processes for removing iron. In groundwater, under anaerobic conditions, iron is present as soluble  $\text{Fe}^{2+}$  ions; these must be oxidised by aeration to insoluble  $\text{Fe}^{3+}$  hydroxides which can then be removed by filtration (DEFRA, n.d.). Iron is normally present in the insoluble oxidised form in surface water and so any suspended solids can be removed via filtration and/or coagulation (DEFRA, n.d.).

The HSE does not consider the use of elemental iron granules will significantly impact the naturally occurring background levels of iron in the aquatic environment. The soil exposure assessment (see 3CP section B.8.2) demonstrates that the soil concentration resulting from the maximum applied dose will be minimal compared to iron naturally present in soil. Any iron from the granules that enters water destined for abstraction either from groundwater or surface water will be effectively treated and removed using existing processes designed for naturally occurring iron compounds. Furthermore, water treatment plants are likely to treat water collected from an entire catchment, if not several catchment areas and so this will dilute the impact of the addition of iron granules. The area to which the plant protection product is applied is unlikely to cover an entire aquifer or catchment. As such, the HSE does not consider it necessary to conduct a specific study into the effects of water treatment processes on the active substance, elemental iron or any of its ions or compounds.

### B.8.3. FATE AND BEHAVIOUR IN AIR

#### B.8.3.1. Route and rate of degradation in air

Elemental iron in solid powdered form is non-volatile. Its vapour pressure is reported as 1 mmHg (converted by HSE to 133.322 Pa) at 1787 °C (Fisher Scientific, n.d.). Therefore, the HSE considers that under ambient environmental conditions, the active substance will not be volatile. Furthermore, it is not considered necessary to calculate an atmospheric  $\text{DT}_{50}$  for elemental iron. The HSE considers it acceptable to waive the data requirements for the fate and behaviour of elemental iron in air.

#### B.8.3.2. Transport via air

The transport of iron via air was not studied and is not required (see section B.8.3.1).

#### B.8.3.3. Local and global effects

The local and global atmospheric effects of iron are considered negligible (see section B.8.3.1).

##### B.8.3.3.1 POPs/PBT assessment

Elemental iron and its oxidation states ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions) are naturally ubiquitous in all environmental compartments. The HSE does not consider the applied active substance will behave differently in the environment from naturally occurring iron or iron compounds. Iron is a metal and does not degrade as such and so could be classified as persistent; however, the intended applied amounts are negligible compared to background levels. The  $\text{PEC}_{\text{SOIL}}$  accumulation value based on 20 consecutive years without tillage is 12.8

mg/kg which is considerably less than the range naturally observed in UK and European soils (140- 22,300 mg/kg) (see section 3CP B.8.2.). Furthermore, according to Annex XIII of the ECHA (2017) Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB assessment (version 3.0), consideration as a Persistent Bioaccumulative or Toxic (PBT) substance or very persistent and very bioaccumulative (vPvB) substance is not required for inorganic substances. Moreover, it is not appropriate to assess iron as an inorganic substance against criteria for classification as a Persistent Organic Pollutant (POP).

#### B.8.4. DEFINITION OF THE RESIDUE

##### B.8.4.1. Definition of the residue for risk assessment

<i>Compartment</i>	<i>Residue/(s)</i>
Soil	Elemental iron (Fe), ferrous iron (Fe <sup>2+</sup> ), ferric iron (Fe <sup>3+</sup> )
Surface Water	Elemental iron (Fe), ferrous iron (Fe <sup>2+</sup> ), ferric iron (Fe <sup>3+</sup> )
Sediment	Elemental iron (Fe), ferrous iron (Fe <sup>2+</sup> ), ferric iron (Fe <sup>3+</sup> )
Ground Water	Elemental iron (Fe), ferrous iron (Fe <sup>2+</sup> ), ferric iron (Fe <sup>3+</sup> )
Air	N/A

##### B.8.4.2. Definition of the residue for monitoring

<i>Compartment</i>	<i>Residue/(s)</i>
Soil	N/A Elemental iron and its two oxidation states are naturally occurring compounds
Sediment	N/A Elemental iron and its two oxidation states are naturally occurring compounds
Water - Surface	N/A Elemental iron and its two oxidation states are naturally occurring compounds
Water – Drinking/Ground	N/A Elemental iron and its two oxidation states are naturally occurring compounds
Air	N/A Elemental iron and its two oxidation states are naturally occurring compounds

#### B.8.5. MONITORING DATA CONCERNING FATE AND BEHAVIOUR OF THE ACTIVE SUBSTANCE, METABOLITES, DEGRADATION AND REACTION PRODUCTS

The HSE considers it acceptable for monitoring data to not be provided for a new active substance. Furthermore, in the case of elemental iron it would be difficult to distinguish the applied active substance from the iron existing in the environment, either from natural sources or derived from human activity. Therefore, it is considered acceptable to waive the requirements for monitoring.

#### B.8.6. REFERENCES RELIED ON

##### B.8.6.1. Literature Review

The applicant has conducted a literature review according to the requirements of Regulation (EU) No. 283/2013, which refers to Article 8(5) of Regulation (EC) No 1107/2009. The applicant also states that the search was conducted following the ECPA ‘Technical guidance on the application of the EFSA Guidance Document “Submission of scientific peer-reviewed open literature for the approval of pesticide active substances under Regulation (EC) 1107/2009”’.

The applicant conducted a single literature review encompassing all areas of the assessment: Toxicology; Ecotoxicology; Metabolism; Residues and Environmental Fate and Behaviour. The search was designed to capture any data published between January 2006 and November 2016. A top-up search was conducted to cover the period from November 2016 to December 2017.

The table below shows the databases used by the applicant to perform the search. The HSE considers that a reasonable number of databases have been used and several of these are directly relevant to Environmental Fate and Behaviour. In particular, the ‘AGRICOLA’, ‘Analytical Abstracts’, ‘CAB ABSTRACTS’, and ‘Environment Abstracts’ cover environmental related topics.

Table 3CA B.8.6.1-1 Databases used/ search engines

Database	Applicant's Justification	Subject coverage
AGRICOLA	Consists of worldwide literature citations for journal articles, monographs, proceedings, theses, patents, translations, audio-visual materials, computer software, and technical reports pertaining to all aspects of agriculture and related fields.	<ul style="list-style-type: none"> <li>-Agriculture (general)</li> <li>- Agriculture (products, engineering, information systems)</li> <li>- Animal sciences</li> <li>-Biotechnology</li> <li>-Botany</li> <li>- Chemical conservation</li> <li>- Cytology</li> <li>- Agricultural economics, energy, entomology, and history</li> <li>- Farm management</li> <li>- Feed science</li> <li>-Fertilisers</li> <li>- Fibre and textiles</li> <li>- Food and nutrition</li> <li>- Forestry</li> <li>- Horticulture</li> <li>- Human ecology</li> <li>- Human nutrition</li> <li>- Hydrology</li> <li>- Microbiology</li> <li>- Natural History</li> <li>- Natural resources</li> <li>- Pesticides</li> <li>- Physiology</li> <li>- Plant sciences</li> <li>- Pollution</li> <li>-Public health</li> <li>- Rural sociology</li> <li>- Soil sciences</li> <li>- Veterinary medicine</li> <li>- Water quality</li> <li>- Weather and climate</li> <li>- Wildlife</li> <li>- Zoology</li> </ul>
Analytical Abstracts	Covers all aspects of analytical chemistry in a wide variety of areas including general applications, biochemistry and clinical chemistry, industrial and applied science, environmental science, agriculture and food, pharmaceuticals and instrumentation.	<ul style="list-style-type: none"> <li>- General</li> <li>- Inorganic</li> <li>- Organic</li> <li>- Industrial</li> <li>- Biochemical</li> <li>- Pharmaceutical</li> <li>- Food</li> <li>- Agricultural and environmental</li> <li>- Computer handling of analytical data</li> <li>- Instrumentation</li> </ul>
BIOSIS ® Toxicology	Subset of BIOSIS ® Previews with a focus on toxicology and related topics. Records are drawn from journal articles, conference papers, monographs and book chapters, notes, letters, and reports, as well as original research. U.S. patent records are also included.	<ul style="list-style-type: none"> <li>-Agriculture</li> <li>- Bacteriology</li> <li>-Biochemistry</li> <li>- Biophysics</li> <li>- Biotechnology</li> <li>-Botany</li> <li>- Cell biology</li> <li>- Clinical medicine</li> <li>- Drugs</li> <li>- Environmental biology</li> <li>- Environmental science</li> </ul>

Database	Applicant's Justification	Subject coverage
		<ul style="list-style-type: none"> <li>- Experimental medicine</li> <li>- Genetics</li> <li>- Immunology</li> <li>- Microbiology</li> <li>- Nutrition</li> <li>- Occupation health</li> <li>- Parasitology</li> <li>- Pathology</li> <li>- Pharmacology</li> <li>- Physiology</li> <li>-Public health</li> <li>- Radiation Biology</li> <li>- Systematic biology</li> <li>- Veterinary science</li> <li>- Virology</li> </ul>
CAB Abstracts	Coverage of worldwide literature on agriculture and allied fields, including veterinary medicine, human nutrition, horticulture, forestry, leisure, recreation, recreation and tourism, crop science, crop protection, breeding and genetics, animal production, animal nutrition, parasitology, soils, land use, agricultural engineering, agricultural economics, and biotechnology. Publication types are journals, monographic series, theses, technical reports, conferences, selected patents, books and annual reports.	<ul style="list-style-type: none"> <li>-Agricultural biotechnology</li> <li>- Agricultural economics and rural sociology</li> <li>- Agricultural engineering</li> <li>- Animal health and veterinary medicine</li> <li>- Animal production and genetics</li> <li>-Biodeterioration and biodegradation</li> <li>- Crop production</li> <li>- Crop protection</li> <li>- Dairy science</li> <li>- Environmental degradation, conservative and amelioration</li> <li>- Forestry</li> <li>- Genetic resources</li> <li>- Horticulture</li> <li>- Human nutrition and diet-related disorders</li> <li>- Human parasitic diseases</li> <li>- Leisure, recreation and tourism</li> <li>- Plant breeding and genetics</li> <li>- Postharvest science</li> <li>- Rural development</li> <li>- Soil science</li> <li>- Sugar industry</li> </ul>
Embase ®	Bibliographic coverage of literature on drugs and pharmacology and all other aspects of human medicine and related discipline. Embase is a key resource for biomedical evidence, from published, peer-reviewed literature, in-press publications and conference abstracts.	<ul style="list-style-type: none"> <li>- Drug research</li> <li>- Pharmacology</li> <li>- Pharmacoeconomics</li> <li>- Pharmaceuticals</li> <li>- Toxicology</li> <li>- Human medicine</li> <li>- Basic biological research</li> <li>- Health policy and management</li> <li>- Public, occupational and environmental health</li> <li>- Substance dependence and abuse</li> <li>- Psychiatry</li> <li>- Forensic science</li> <li>- Biomedical engineering and instrumentation</li> <li>- Medical devices</li> </ul>
Environment Abstracts	Encompasses all aspects of the impact of people and technology on the environment and the effectiveness of remedial policies	<ul style="list-style-type: none"> <li>-Agriculture</li> <li>- Air pollution</li> <li>-Control technologies</li> </ul>



Database	Applicant's Justification	Subject coverage
	and technologies. The database covers journals, conference papers and proceedings, special reports from international agencies, non-governmental organisations, universities, associations and private corporations. Other materials selectively indexed include significant monographs, government studies and newsletters.	<ul style="list-style-type: none"> <li>-Endangered species</li> <li>- Energy</li> <li>- Environmental design</li> <li>- Environmental education</li> <li>- Environmental law and policy</li> <li>- Environmental safety</li> <li>- Geophysical and climate science</li> <li>- Global warming</li> <li>- International environmental policy</li> <li>- Land use and pollution</li> <li>- Marine pollution</li> <li>- Noise pollution</li> <li>- Population</li> <li>- Population studies</li> <li>- Radiological contamination</li> <li>- Resource management</li> <li>- Solid and toxic waste</li> <li>- Sustainable development</li> <li>- Toxicological effects</li> <li>- Transportation</li> <li>- waste management</li> <li>- Water pollution</li> <li>- Wildlife/ biodiversity</li> </ul>
Medline ®	US National Library of Medicine premier bibliographic database. It contains references to journal articles in life sciences with a concentration on biomedicine and health. This is broadly defined to encompass those areas of the life sciences, behavioural sciences, chemical sciences, and bioengineering need by health professionals and other engaged in basic research and clinical are, public health, health policy development, or related educational activities. Medline also covers life science vital to biomedical practitioners, researchers, and educators, including aspects of biology, environmental science, marine biology, plant and animal science as well as biophysics and chemistry.	<ul style="list-style-type: none"> <li>- Clinic and preclinical medicine</li> <li>- Dentistry</li> <li>- Nursing</li> <li>- Population and reproductive biology</li> <li>- Pharmacology and pharmaceuticals</li> <li>- Psychiatry and psychology</li> <li>- Environmental, public and occupational health</li> <li>- Veterinary medicine</li> <li>- Nutrition</li> <li>- Pathology</li> <li>- Anatomy and physiology</li> <li>- Toxicology</li> <li>- Genetics</li> <li>- Microbiology</li> <li>- Pathology</li> <li>- Biomedical technology</li> <li>- Health planning and administration</li> <li>- Space life science</li> </ul>
Toxfile ®	Covers the toxicological, pharmacological, biochemical and physiological effects of drugs, pesticides and other chemicals. Typical areas of coverage include drug reactions, chemically induced diseases, carcinogenesis, mutagenesis, teratogenesis, environmental pollution, waste disposal, radiation, and food contamination.	<ul style="list-style-type: none"> <li>- Adverse drug reaction</li> <li>- Air pollution</li> <li>- Animal venom</li> <li>- Antidotes</li> <li>- Carcinogenesis via chemicals</li> <li>- Chemically induced diseases</li> <li>- Drug evaluation</li> <li>- Environmental pollution</li> <li>- Food contamination</li> <li>- Metagenesis</li> <li>- Occupation</li> <li>- Pesticides</li> <li>- Radiation</li> <li>- Teratogenesis</li> <li>- Toxicology</li> </ul>



Database	Applicant's Justification	Subject coverage
		- Waste disposal
Toxicology Abstracts	Covers issues from social poisons and substance abuse to natural toxins, from legislation and recommended standards to environmental issues.	<ul style="list-style-type: none"> <li>- Pharmaceuticals</li> <li>- Food, additives and contaminants</li> <li>- Agrochemicals</li> <li>- Cosmetics, toiletries and household products</li> <li>- Industrial chemicals</li> <li>- Metals</li> <li>- Toxins and other natural substances</li> <li>- Social poisons and drug abuse</li> <li>- Polycyclic hydrocarbons</li> <li>- Nitrosamines and related compounds</li> <li>- Radiation and radioactive materials</li> <li>- Methodology</li> <li>- Legislation and recommended standards</li> </ul>
TOXLINE ®	Toxicology reference database that provides bibliographic information for journal articles on the effects of drugs and other chemicals.	<ul style="list-style-type: none"> <li>- Biochemistry</li> <li>- Pharmacology</li> <li>- Physiology</li> <li>- Toxicology</li> </ul>
TRACE	Includes information from peer-reviewed toxicology and nutrition journals as well as secondary sources and websites.	- Chemical toxicology

#### *Search strategy and terms*

The applicant implemented a single concept search strategy, using the CAS RN number (7439-89-6) for iron, its synonyms and name fragments, along with the form-specific term “powder”. This approach captured all data for all subject areas in a single search rather than using separate focused searches. Either approach is acceptable according to the EFSA 2011 guidance for submission of scientific peer-reviewed open literature.

Table 3CA B.8.6.1-2 Search terms used for the single concept search strategy for elemental iron

Subject areas	Search terms
Toxicology, metabolism, residues, environmental fate and behaviour, ecotoxicology.	(“7439-89-6” or “iron” or “Ancor B” or “Ancor en 80/150” or “Armco iron” or “Atomel 28” or “Atomel 300M200” or “Atomel 500M” or “Atomel 95” or “Atomiron 44MR” or “Atomiron 5M” or “Atomiron AFP 25” or “Atomiron AFP 5” or “ATW 230” or “ATW 432” or “carbonyl iron” or “DSP 1000” or “DSP 1288” or “DSP 135” or “DSP 135C” or “DSP 138” or “EF 1000” or “EF 250” or “EFV 200/300” or “EFV 250” or “EFV 250/400” or “EO 5A” or “Ferronyl” or “Ferrous iron” or “Ferrovac E” or “Ferrum” or “GS 6” or “Hoeganaes EH” or “NC 100” or “PZh-1M3” or “PZh-2” or “PZh1M1” or “PZh2M” or “PZh2M1” or “PZh2M2” or “PZh3” or “PZh3M” or “PZh4M” or “PZhO” or “Remko” or “SUY-B 2” or “E1UOL152H7”) AND (powder)

The HSE considered that the specific term for the active substance i.e. “elemental iron” should be included in the search strategy for completeness. Furthermore, the HSE considered that as pure iron (Fe) is highly likely to form ionic compounds in the presence of water and oxygen under environmental conditions, this should be taken into consideration in the search terms selected. The following question was asked:

*Please include the search terms “ferric” and “elemental iron” in the search strategy.*

*Specific points to address in reply to HSE CRD request: It is not considered appropriate to exclude all forms of iron other than pure iron powder from the search. As you have noted in the dossier, elemental iron (Fe) is highly likely to oxidise to ferric iron (Fe 3+) in the natural environment and oxides or hydroxides under mammalian physiological conditions. Therefore, the HSE evaluator considers the term “ferric” should also be included in the search strategy. Please also include the specific name of the active substance for which approval is being sought (elemental iron).*

**Applicant’s response:**

*“Preliminary searches on the term “elemental iron” for the date range specified in the existing Literature Review Report (LRR) (excluding references already identified by the searches described in the LRR) indicate that slightly more than 500 references would require a rapid filter for potential relevance.*

*However, similar searches using the term “ferric” returns nearly 80,000 references requiring rapid filter. This would be a substantial undertaking requiring several months to consider the titles only and produce a “short-list” of potentially relevant references. (Please note that this is a preliminary stage, and further work would subsequently be required to evaluate the “short-list”, on the basis of abstract and/or full text, for relevance and reliability)*

*It may be worth considering at this stage that “ferric” is not a particularly useful search term, in that it will not necessarily identify references relevant to iron in its 3+ oxidation state. For example, ferric oxide would (arguably) be more commonly referred to as “iron oxide”; ferric hydroxide as “iron hydroxide”; therefore, searches for “ferric” would not necessarily identify all the publications that use those terms to identify the test substance. To avoid this pitfall, we would recommend a different approach – this is, the identification of specific compounds and/or physical forms of interest, for which the searches to be undertaken would include CAS Registry Numbers.*

*We would be pleased to discuss this with you and hear your opinion about the above.”*

The HSE has requested that the additional 500 references identified in a preliminary search for the specific term ‘elemental iron’ are considered in the literature review for completeness. The results of the search process for the specific term ‘elemental iron’ are included in table 3CA B.8.6.1-6. The HSE accepts that including the references for ‘ferric’ would be cumbersome and not materially add to the assessment. The more mobile and consequently more bioavailable and toxic form of iron, ferrous iron, is included in the search.

### *Initial rapid assessment*

The applicant carried out an initial rapid assessment of relevance, using the titles of publications alone. Anything considered to have potential relevance (including tenuous, fleeting or even undecipherable relevance) to the fields of environmental fate, toxicology, ecotoxicology, metabolism or residues, were not rejected at this stage.

### *Criteria for relevance*

Of those publications deemed to be of potential relevance, the applicant considered the abstract to conclude whether the publication was either ‘relevant’ or ‘reliable’. For some studies, the applicant considered it necessary to view the full text in order to come to a conclusion. The applicant used the following criteria for relevance when selecting studies related to environmental fate and behaviour:

- Well-defined test material applied as active substance solution/suspension or plant protection product (excluding salts and other iron compounds)
- Appropriate substrate (i.e. type of soil- a standard substrate, or a non-standard substrate if it would be applicable to a particular intended use)
- No previous contamination of the substrate

- Exposure of the substrate through active substance applied as a solution/suspension or as a commercial formulation, no mixtures with other active substances
- Application rates and/or substrate loads which are representative of those expected under current intended uses and (if applicable) appropriate associated endpoint derivation(s)
- Test conditions representative of European geoclimatic conditions
- Information that informs or partially informs data requirements, relating to environmental fate and behaviour.

The HSE considers the relevance criteria acceptable: it is appropriate for articles to reference environmental substrate under European conditions. Furthermore, the test substance should be well defined and at a concentration relevant to the intended use. The HSE is uncertain of the point “no previous contamination of the substrate” given that iron is a ubiquitous element, naturally occurring in all environmental compartments. The HSE considers this to mean severely contaminated land (e.g. previous pollution via heavy industry or following accidental contamination) was not considered in the literature review.

#### *Criteria for reliability*

The following reliability criteria were used to assess any environmental fate and behaviour articles that were deemed relevant. The applicant used the reliability indicators based on the guidance of Mensink et al. (2008).

Table 3CA B.8.6.1-3 Reliability scores used to assess relevant environmental fate and behaviour studies

Reliability indicator	Description	Definition
Ri 1	Reliable without restrictions	All critical reliability criteria for this study are fulfilled. The study is well designed and performed, and it does not contain flaws that affect the reliability of the study.
Ri 2	Reliable with restrictions	The study is generally well designed and performed, but some minor flaws in the documentation or set-up may be present.
Ri 3	Not reliable	Not all critical reliability criteria for this study are fulfilled. The study has clear flaws in the study design and/ or how it was performed.
Ri 4	Not assignable	Information needed to assess the study is missing. This concerns studies that do not give sufficient experimental details and that are only listed in abstracts or secondary literature (books, reviews etc.) or studies of which the documentation is not sufficient for assessment of reliability for one or more vital parameters.

The HSE is not familiar with the reliability scores proposed by Mensink et al. (2008) and therefore asked the following question to the applicant:

*Please explain and justify the use of the reliability scores used for Environmental Fate and Ecotoxicology i.e. Mensink et al. (2008) and Moermond et al. (2016)?*

**Applicant's response:**

*"For mammalian toxicology, it is standard industry practice to apply the criteria published by Klimisch et al. (1997) in order to provide a "weighting" as to the reliability of each set of experimental results. However, "mammalian toxicology" is a relatively narrow field (for example, there are significantly fewer commonly-used test species) and these criteria are more difficult to apply meaningfully to studies considering environmental and ecotoxicological aspects of chemical behaviour. This is due to, among other factors, the nature and variety of the methodology that can be employed and the conclusions that can (and cannot) be drawn or inferred. Therefore, for studies in these fields, an adaptation of the Klimisch criteria is typically employed (Mensink et al. 2008; Moermond et al. 2016). This serves the same purpose as the Klimisch criteria, as applied to mammalian toxicology, in that it gives individual studies a "weighting" as to the reliability and significance of the effects observed in the context of environmental fate/ecotoxicity risk assessment."*

The HSE accepts this justification. It is noted that in the EFSA Q+A for June 2019, EFSA indicated that the Klimisch criteria can be considered for the assessment of reliability. Therefore, the HSE considers the use of Mensink et al. (2008) which is based on Klimisch to be acceptable.

The number of records retrieved for each stage of the process are shown below for the main review (2006 to 2016) and the top-up review (2016 to 2017) in tables 3CA B.8.6.1-6 and -7 respectively. A total of 14 studies were considered relevant and reliable. However, none of these studies were related to environmental fate. The HSE considers the literature review of elemental iron to be acceptable.

Table 3CA B.8.6.1-4 Results of the study selection process for elemental iron (includes Environmental Fate, Ecotoxicology, Residues, Metabolism and Toxicology) covering the period from 2006 until November 2016

Stage of study selection process (main review)	Number of summary records retrieved
Total number of summary records retrieved:	11,002
Number of summary records excluded from the search results after rapid assessment for relevance:	10,609
Total number of summary records remaining after filtering out those of clear irrelevance and manual de-duplication:	393
Total number of full-text documents assessed in detail:	38
Number of studies excluded from further consideration after detailed assessment for relevance and/or reliability:	24
Number of studies not excluded for relevance or reliability after detailed assessment:	14
Number of studies not excluded for relevance or reliability after detailed assessment, that were relevant to the environmental fate assessment:	0

Table 3CA B.8.6.1-5 Results of the study selection process for elemental iron (includes Environmental Fate, Ecotoxicology, Residues, Metabolism and Toxicology) covering the period from 28th November 2016 until 18<sup>th</sup> December 2017

Stage of study selection process (top-up review)	Number of summary records retrieved
Total number of summary records retrieved:	2145
Number of summary records excluded from the search results after rapid assessment for relevance:	2061
Total number of summary records remaining after filtering out those of clear irrelevance and manual de-duplication:	84
Total number of full-text documents assessed in detail:	6
Number of studies excluded from further consideration after detailed assessment for relevance and/or reliability:	6
Number of studies not excluded for relevance or reliability after detailed assessment:	0
Number of studies not excluded for relevance or reliability after detailed assessment, that were relevant to the environmental fate assessment:	0

Upon request of the HSE, the applicant performed an additional literature review for the specific term ‘elemental iron’. The search process used (i.e. databases, relevance criteria and reliability criteria) was identical to that described above for the main literature review. Out of the five records not excluded for relevance or reliability, none were considered relevant for environmental fate. The HSE considers this additional search acceptable and notes this has no impact on the outcome of the environmental fate risk assessment.

Table 3CA B.8.6.1-6 Results of the study selection process for elemental iron (includes Environmental Fate, Ecotoxicology, Residues, Metabolism and Toxicology) for the specific term ‘elemental iron’ performed in November 2019

Stage of study selection process (for specific term ‘elemental iron’)	Number of summary records retrieved
Total number of summary records retrieved:	710
Number of summary records excluded from the search results after rapid assessment for relevance:	431
Total number of summary records remaining after filtering out those of clear irrelevance and manual de-duplication:	279
Total number of full-text documents assessed in detail:	37
Number of studies excluded from further consideration after detailed assessment for relevance and/or reliability:	31
Number of studies not excluded for relevance or reliability after detailed assessment:	5*
Number of studies not excluded for relevance or reliability after detailed assessment, that were relevant to the environmental fate assessment:	0

\* Applicant’s text: “This figure is not “6”, as may be expected from taking into account the two rows directly above. This is because a single study not “excluded” after detailed assessment (Yameen *et al.*, 2013), and summarised in Appendix S3a, was nevertheless eventually awarded an evaluation indicating that it did not achieve a suitable standard of reliability (“Klimisch score 4 - not assignable”).”

## B.8.6.2 Studies relied upon in the assessment

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
B.8	World Health Organisation	2003	<i>Iron in drinking water: Background document for development of WHO Guidelines for Drinking-water Quality.</i> [online] Available at: <a href="https://www.who.int/water_sanitation_health/dwg/chemicals/iron.pdf">https://www.who.int/water_sanitation_health/dwg/chemicals/iron.pdf</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Brady, N.	1990	<i>The Nature and Properties of Soils.</i> 10 <sup>th</sup> ed. Macmillan: New York. Non- GLP Published	N	N	N/A	-	N/A
B.8.1	British Geological Survey	n.d	UK soil observatory maps. Available at: <a href="http://mapapps2.bgs.ac.uk/ukso/home.html">http://mapapps2.bgs.ac.uk/ukso/home.html</a> Non- GLP Published	N	N	N/A	-	N/A
	Chemistry Libretexts	2019	<i>Pourbaix diagram for iron.</i> Available at: <a href="https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chem_1_(Lower)/16%3A_Electrochemistry/24.04%3A_The_Nernst_Equation">https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chem_1_(Lower)/16%3A_Electrochemistry/24.04%3A_The_Nernst_Equation</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Fageria, N.K, Baligar, V.C and Wright, R.J.	1990	Iron nutrition of plants: an overview on the chemistry and physiology of its deficiency and toxicity. In <i>Pesq. Agropec. Bras., Brasflia</i> , 25(4), pp. 553-570 [pdf] Available at: <a href="https://pdfs.semanticscholar.org/13bd/a621f735e9d4d297e8d1cd869e9eedd68cc4.pdf">https://pdfs.semanticscholar.org/13bd/a621f735e9d4d297e8d1cd869e9eedd68cc4.pdf</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Pérez-Guzmán, L., Bogner, K. R. & Lower, B. H.	2010	Earth's Ferrous Wheel. In <i>Nature Education Knowledge</i> 3(10):32. Available at:	N	N	N/A	-	N/A

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			<a href="http://www.nature.com/scitable/knowledge/library/earth-s-ferrous-wheel-15180940/">http://www.nature.com/scitable/knowledge/library/earth-s-ferrous-wheel-15180940/</a> Non- GLP Published					
B.8.1	Rawlins, B. G., McGrath, S. P., Scheib, A. J., Breward, N., Cave, M., Lister, T. R., Ingham, M., Gowing, C. and Carter, S.	2012	<i>The Advanced Soil Geochemical Atlas of England and Wales</i> [e-book]. Available at: <a href="https://www.bgs.ac.uk/GBASE/advSoilAtlasEW.html">https://www.bgs.ac.uk/GBASE/advSoilAtlasEW.html</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Scheffer, F. & Schachtschabel, P.	1992	<i>Lehrbuch der Bodenkunde</i> (textbook of soil science). Springer: Berlin. Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Vance, D.B.	1994	Iron- The environmental impact of a universal element. In <i>National Environmental Journal</i> , 4(3), pp. 24-25 [online]. Available at: <a href="https://cluin.org/conf/tio/ISM1_021612/Vance-FeO-complexation-of-pollutants-web-article-2010.pdf">https://cluin.org/conf/tio/ISM1_021612/Vance-FeO-complexation-of-pollutants-web-article-2010.pdf</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Vitosh, M.L., Warncke, D.D. and Lucas, R.E	1994	Secondary and micronutrients for vegetables and field crops. Michigan State University. [pdf] Available at <a href="https://msu.edu/~warncke/E0486.pdf">https://msu.edu/~warncke/E0486.pdf</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.1	Weber, K.A., Achenbach, L.A. & Coates, J.D.	2006a	Microorganisms pumping iron: Anaerobic microbial iron oxidation and reduction. In <i>Nature Reviews Microbiology</i> (4), pp. 752-764 [online]. Available at: doi: 10.1038/nrmicro1490 Non- GLP	N	N	N/A	-	N/A

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Published					
B.8.2	Kappler, A., Benz, M., Schink, B. and Brune, A	2004	Electron shuttling via humic acids in microbial iron (III) reduction in freshwater sediment. In <i>FEMS Microbiology Ecology</i> , 47(1), pp. 85–92 [online] Available at: <a href="https://doi.org/10.1016/S0168-6496(03)00245-9">https://doi.org/10.1016/S0168-6496(03)00245-9</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.2	King, G.M. & Garey, M.A.	1999	Ferric iron reduction by bacteria associated with the roots of freshwater and marine macrophytes. In <i>Applied and environmental microbiology</i> , 65(10), pp. 4393–4398 [online]. Available at: <a href="https://aem.asm.org/content/aem/65/10/4393.full.pdf">https://aem.asm.org/content/aem/65/10/4393.full.pdf</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.2	Lovley, D.R. & Phillips, E.J.P	1986	Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac river. In <i>Applied and environmental microbiology</i> , 52(4), pp. 751-757 [online]. Available at: <a href="https://www.ncbi.nlm.nih.gov/pmc/articles/PMC239109/">https://www.ncbi.nlm.nih.gov/pmc/articles/PMC239109/</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.2	Weber, K.A., Urrutia, M.M., Churchill, P.F., Kukkadapu, R.K. & Roden, E.E.	2006b	Anaerobic redox cycling of iron by freshwater sediment microorganisms. In <i>Faculty Publications in the Biological Sciences</i> . 217 [online]. Available at <a href="http://digitalcommons.unl.edu/bioscifacpub/217">http://digitalcommons.unl.edu/bioscifacpub/217</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.2	Xing, W & Liu, G	2011	Iron biogeochemistry and its environmental impacts in freshwater lakes. In	N	N	N/A	-	N/A



Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			<i>Fresenius Environmental Bulletin</i> 20(6) pp.1339-1445.[online Available at <a href="https://www.researchgate.net/publication/236267914_Iron_biogeochemistry_and_its_environmental_impacts_in_freshwater_lakes">https://www.researchgate.net/publication/236267914_Iron_biogeochemistry_and_its_environmental_impacts_in_freshwater_lakes</a> ] Non- GLP Published					
B.8.2.3.1	DEFRA	n.d	<i>Drinking Water Inspectorate</i> Chapter 5- Water treatment processes [pdf]. Available at: <a href="http://dwi.defra.gov.uk/private-water-supply/installations/Treatment-processes.pdf">http://dwi.defra.gov.uk/private-water-supply/installations/Treatment-processes.pdf</a> Non- GLP Published	N	N	N/A	-	N/A
B.8.3.1	Fisher scientific	n.d	Safety Data Sheet: Iron Powder [online]. Available at: <a href="https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-i/S25370A.pdf">https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-i/S25370A.pdf</a> Non- GLP Published	N	N	N/A	-	N/A

### B.8.7. APPENDIX

Description of how samples were collected and analysed for the UK soil observatory database of topsoil iron concentrations in England and Wales (refers to DAR Figure 3CA B.8.1.1-1; UK Soil Observatory, no date.)

The concentrations of iron were determined using wavelength dispersive X-ray fluorescence spectrometry with a lower limit of detection of 0.0049% and typical coefficients of variation of around 1% for repeated analyses of certified reference materials. The coefficient of variation (CV) expresses the error associated with subsampling and analysis; CV values of less than around 10% suggest that analyses are reasonably accurate.

National Soil Inventory (NSI) data is a set of point data. NSI data covers England and Wales on a 5 km grid and provides detailed information for each intersect of the grid. Collectively NSI data are statistically representative of England and Wales soils and they offer a valuable foundation for future monitoring of soil quality. The original sampling was from around 1980 and there have been partial resamplings in the mid-1990s.

The Advanced Soil Geochemical Atlas of England and Wales was a joint project between the British Geological Survey (BGS) and Rothamsted Research and is based on soil samples collected for the National Soil Inventory

(NSI) by the Soil Survey for England and Wales (now the National Soil Resources Institute, Cranfield University). The maps are based on 5700 surface soil samples (0-15 cm), collected across England and Wales, that have been analysed for 52 major and trace elements. The compiled atlas is available as an [e-book](#). The method for sample collection, processing and analysis is described within this e-book (Rawlins *et al.*, 2012) and is copied below.

## Sampling and sample preparation

Soil sampling took place between 1978 and 1982 and was restricted to the uppermost 15 cm of *mineral* soil (or less if rock intervened), or of peat, as appropriate, i.e. litter layers were not sampled, as they were regarded as ephemeral. The actual sampling depth was recorded. Twenty-five cores of soil were taken at the nodes of a 4 m grid within a 20 m x 20 m square centred on each OS 5-km grid point across England and Wales. A total of 5691 samples were collected; large urban areas were avoided. The cores were taken with a screw-type, mild-steel auger, to avoid contamination from traces of elements such as chromium and manganese present in stainless, plated or similar special steels. The cores of soil were bulked and mixed well in the field, double-bagged in food-grade polythene bags, and a waterproof and rot-proof label ('Synteape') placed between the bags. The target sample mass was 450 g of air-dried soil. In organic or other loosely packed layers, it was often necessary to take many more than 25 auger cores. In such cases, the interval of the subsampling grid decreased in 1 m steps (e.g. 3 m x 3 m) and the whole grid resampled. This procedure was repeated until sufficient soil was judged to have been taken.

Field-moist samples of soil were refrigerated (to 4°C) on the day of sampling, and transported to the Soil Survey laboratory within the following two weeks. On receipt, each sample was allocated a unique sample number, cross-referenced to the National Grid reference of the site. Samples were spread out on sheets of 'Kraft' paper to air-dry, after which each was split into two equal portions. One of these was kept as a reference sample, without further treatment, in case of contamination or loss during subsequent analysis. The other sample was milled in a mild-steel roller-mill to pass a 2-mm aperture sieve. Preliminary work had shown that no detectable contamination of the samples arose from this procedure. A further 25 g subsample was taken from the <2 mm air-dry sample by coning and quartering, and ground to <150 micrometres in an all-agate planetary ball mill. These samples were transferred to the BGS laboratories for determination of total element concentrations by X-Ray Fluorescence Spectrometry (XRFS). At the sample preparation facility, BGS, Keyworth, a 10 g subsample of milled material was mixed thoroughly with 3 g of binder for three minutes in an agate planetary ball mill. This mixture was then pressed into a 32 mm diameter pellet at 250 kN using a Herzog (HTP-40) semi-automatic press. The binder consists of nine parts EMU120FD styrene co-polymer (BASF plc) and one part Ceridust 3620, a micronised polyethylene wax (Hoechst), after van Zyl (1982).

Around thirty years have passed since the samples were taken, and in that time they were stored air dry. It is unlikely that any changes took place in the total concentrations of the elements that were determined in this advanced analysis. In that time it is unlikely also that the concentrations of most of the elements have changed markedly at the field sites. Possible exceptions are the plant nutrients Ca, K, Mg, P and S which are often added in fertilisers or liming materials, and in the

case of S, any sulphates added to soil rapidly wash out under most conditions. Examples of those elements that do not change rapidly are Co, Ni and V where soil samples were retaken some 15 years later in the Humber–Trent region. The mean and median concentrations measured varied little between the two dates, often within the limit of expected analytical variation (Lark et al, 2006). This reanalysis therefore provides a good benchmark for the concentrations of most of the elements determined in the soils of England and Wales that is unlikely to have been altered by such processes as natural or industrially derived deposition from the atmosphere or the deposition of waste materials, which tends to be localised.

## Analysis

Major, minor and trace-element determinations for the NSI samples were carried out by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRFS) and energy-dispersive (polarised) X-ray fluorescence spectrometry (ED-P-XRFS) (Ingham and Vrebos, 1994). A Philips *MagiX PRO* and a PANalytical *Axios Advanced* sequential wavelength-dispersive x-ray fluorescence spectrometer both fitted with rhodium-anode X-ray tubes (4 kW 60 kV) were used for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Nd, Sm, Yb, Hf, Ta, W, Tl, Pb, Bi, Th and U. The spectrometers were controlled using PANalytical *SuperQ* application software package, version 4.00, running under MicroSoft™ WindowsXP Pro operating system. A PANalytical *Epsilon5* energy-dispersive, polarised, x-ray fluorescence spectrometer fitted with a gadolinium-anode X-ray tube (600 W 100 kV) was used for Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, and Ce. The PANalytical *Epsilon5* was controlled using *Epsilon5* application software package, version 2.0A, running under MicroSoft™ WindowsXP Pro operating system.

Reported values of the lower limit of detection (LLD) for each element are listed in Table 1. To achieve improved LLDs for Se and Tl, the channel analysis times were increased significantly. This yielded an improvement in LLDs of 0.1 and 0.15 mg/kg respectively. The ED-XRFS analytes were also adjusted, improving the LLDs for example for Cd from 0.5 to 0.25 mg/kg. Conversely, channel counting times were decreased for As, Nd and Hf with a reduction of LLDs of 1.5, 1.4 and 1 mg/kg respectively. Remaining LLDs for major elements reflect the standard values routinely reported

for soil and sediment samples analysed for the Geochemical Baseline Survey of the Environment (G-BASE) project.

**Table 1** Values of lower limit of detection (LLD) for all elements (mg/kg, or where stated %).

Element	LLD	**Method	Element	LLD	**Method
Ag	0.25	ED-XRFS	*Ni	1.3	WD-XRFS
*Al (%)	0.05	WD-XRFS	*P (%)	0.0087	WD-XRFS
*As	2.4	WD-XRFS	*Pb	1.2	WD-XRFS
Ba	0.5	ED-XRFS	Pd	0.25	ED-XRFS
Bi	0.3	WD-XRFS	Rb	0.7	WD-XRFS
Br	0.7	WD-XRFS	S	801	WD-XRFS
*Ca (%)	0.025	WD-XRFS	Sb	0.25	ED-XRFS
*Cd	0.25	ED-XRFS	*Sc	2.4	WD-XRFS
*Ce	0.6	ED-XRFS	Se	0.1	WD-XRFS
*Co	1.5	WD-XRFS	Si (%)	0.023	WD-XRFS
*Cr	2.8	WD-XRFS	Sm	3.0	WD-XRFS
*Cs	0.5	ED-XRFS	*Sn	0.25	ED-XRFS
*Cu	1.2	WD-XRFS	Sr	0.8	WD-XRFS
*Fe (%)	0.0049	WD-XRFS	*Ta	1.1	WD-XRFS
Ga	1.0	WD-XRFS	Te	0.35	ED-XRFS
Ge	0.5	WD-XRFS	Th	0.7	WD-XRFS
Hf	2.0	WD-XRFS	*Th	0.7	WD-XRFS
I	0.35	ED-XRFS	Ti (%)	0.0036	WD-XRFS
In	0.25	ED-XRFS	Tl	0.35	WD-XRFS
*K (%)	0.0066	WD-XRFS	*U	0.7	WD-XRFS
La	0.6	ED-XRFS	*V	2.7	WD-XRFS
*Mg(%)	0.109	WD-XRFS	*W	0.6	WD-XRFS
*Mn (%)	0.0054	WD-XRFS	Y	0.8	WD-XRFS
*Mo	0.2	WD-XRFS	Yb	1.3	WD-XRFS
*Na (%)	0.2	WD-XRFS	*Zn	1.1	WD-XRFS
Nb	0.7	WD-XRFS	*Zr	0.8	WD-XRFS
*Nd	5.0	WD-XRFS			

\* denotes those elements for which a correction factor was applied to ensure the reported analyses were consistent with previous analyses of internal reference materials.

\*\* WD- and ED-XRFS refer to wavelength and energy dispersive X-ray fluorescence spectrometry respectively.

## Data conditioning

Once the data had been checked, verified and accepted from the laboratory analyses, further checks and conditioning of the data was carried out. Data from the reanalysis of NSI samples



underwent two processes. First, comparison with the contemporaneous measurements of both primary and secondary reference materials to quantify analytical accuracy and precision. Second, normalisation and levelling of the data to previous XRF geochemical analyses of geochemical samples from across England and Wales as part of the G-BASE survey (Johnson et al., 2005) which ensures that direct comparisons can be made between the data.

Reference materials (RMs) are samples that have been collected, prepared and analysed according to documented procedures, and analysed repeatedly, to give what become accepted values (Johnson, 2011). Table 2 lists reference materials used during the analysis. Primary reference materials (PRMs) were four international certified standards with recognised and accepted elemental concentrations. Each of these was analysed twice by XRF after each batch of 500 samples. The four secondary reference materials (SRM), also listed in Table 2, were BGS in-house reference samples developed for internal use by the Geochemical Baselines Survey of the Environment (G-BASE) project. These are bulk stream sediments and soil standards collected at various places in the UK. The SRMs were inserted into the NSI samples at a frequency of two standards per 100 samples and importantly, were 'blind' to the laboratory analysts.

**Table 2** Summary information for the reference materials (RMs) included in the XRF analysis.

Primary RMs		Secondary RMs	
ID	Description	ID	Description
GSS-1 (GBW07401)	Soil reference material. National Research Centre for CRMs, Office for China	S15B	Stream sediment reference material. Penrith sandstone, UK
GSS-4 (GBW07404)	Lake sediment reference material from CCRMP*. Composite of two lake sediments from Ontario, Canada.	S57A	Surface soil reference material, UK
LKSD-1	Lake sediment reference material from CCRMP*. Composite of two lake sediments from Ontario, Canada.	S57A	Surface soil reference material, UK
LKSD-4	Lake sediment reference material CCRMP*. Composite of two lake sediments from Ontario and Saskatchewan, Canada.	S58A	Profile soil reference material, UK

\* Canadian Certified Reference Material Project; Natural Resources Canada.

The results of the analysis of the SRMs are crucial for the process of assessing the accuracy of the data and normalisation and levelling of the latter to existing national geochemical datasets. To assess the accuracy, SRM results are checked against accepted values for each element (values

listed in Lister and Johnson, 2005) graphically, using Shewhart control plots. These plots also help to identify any bias in the data, where laboratory batches may need to be levelled using a linear transformation. Levelling is generally required following major changes in analytical procedures and to level new datasets relative to regional-scale geochemical data held by BGS. In such cases, the normalisation of SRM results gives levelling factors that are applied to the data (Lister and Johnson, 2005). Those samples for which the reported values were below the detection limit for each analysis were set to half the detection limit (see Table 1) for creating the maps and calculating summary statistics.

**Table 3** Coefficient of variation (%) for each of the 53 elements from repeated analyses (n=25) of the four certified reference materials (Table 2).

Element	Reference material			
	GSS-1	GSS-6	LKSD-1	LKSD-4
Ag	39	NA	16	49
Al	2.7	2.3	3.4	3.9
As	3.9	2	5	5
Ba	1.2	0.79	1.1	1.3
Bi	20	1.7	41	85
Br	20	5.6	6.7	1.5
Ca	1.2	2.9	1.5	1.2
Cd	2.5	NA	8.9	5.5
Ce	1.3	1.2	2.6	1.9
Cl	25	44	4.2	13
Co	5.9	12	4.9	8.3
Cr	4	2.9	3.5	4.8
Cs	2.4	2.4	18	12
Cu	3.6	1.9	2	3
Fe	0.92	1.5	1.2	1.7
Ga	2.3	3.3	5	5.2
Ge	39	12	75	33
Hf	20	13	32	29
I	6.6	1.6	7.8	2.2
In	29	35	40	33
K	2.9	3.5	3	3.4
La	1.3	1.6	2.5	1.5
Mg	3.5	NA	5.1	4
Mn	2.1	2	2.7	3.3

To provide a quantitative estimate of analytical precision for the XRFS analyses for each element, we calculated the coefficient of variation (CV- %) based on repeated analyses of the four reference materials which were undertaken at regular intervals throughout analyses of all the NSI samples. The CV values are presented in Table 3; in general they indicate that the analytical precision is very good (CV <5%). Larger (>10%) values show that the precision is somewhat poorer and suggests care should be taken in placing too much interpretation on small differences in the reported values for those elements.

To assess analytical precision we can compare the reported values from repeated analyses of reference materials with their certified values. Examples of this are shown in Figure 1 above for Se and Cd. In both cases, the repeated analyses are close to or slightly below the certified values suggesting that the reported values are generally accurate.

### Summary statistics and plots for each element

Summary statistics and plots were created using the R environment (R core team, 2010) and bespoke scripts which include functions from the fBasics and Hmisc packages. Three plots, including a histogram with boxplot, a normal Q-Q plot and cumulative frequency plot as well as a list of descriptive statistics were calculated in R for each element. These are all aligned and displayed on one page for each element.

## Creating the geochemical maps

The geochemical maps were created using the R environment (R core team, 2010) and bespoke scripts which include functions under the 'sp' (Pebesma and Bivand, 2005) and 'gstat' (Pebesma, 2004) packages. For each element, the skewness of its frequency distribution was calculated and if this was greater than 1 the values were log transformed. Distributions for which the skewness was less than 1 were not transformed. Predictions were made on a 2.5 km by 2.5 km grid using the data and by applying inverse distance weighted (IDW) interpolation. A search radius of 30 km was used with a minimum of eight and a maximum of 24 sampling points within this. For those elements which were log transformed, the estimates were back transformed by applying the exponential function ( $e^x$ ).

For each element two maps were plotted. The first uses an arithmetic scale for the colour scheme which separates the distribution into ten arithmetic intervals – this is particularly effective if the data are not strongly skewed as each interval is represented on the map and the each interval is the same. The second map has a percentile scale – in this case the intervals are calculated as the deciles (10th percentile, 20th percentile ... 90th percentile) of the cumulative frequency distribution. This approach is useful if the data are strongly skewed because the colours account for the non-linear variation; the viewer must always remember that the *concentration* intervals are not equal. The advantage of presenting maps in both these forms can be appreciated when considering the maps of cadmium (Cd). The arithmetic map indicates that the largest number of high values occur in Derbyshire (central England), but the subtle variations are obscured when compared to the percentile scale map which highlights other features of the spatial distribution.

The concentrations of the most abundant elements are expressed as percentages in soil (%) whilst the concentrations of those elements of lower abundance are expressed in milligrams per kilogram of soil (mg/kg).