

Review article

Cobalt and secondary poisoning in the terrestrial food chain: Data review and research gaps to support risk assessment[☆]Judit Gál^a, Andrew Hursthouse^{a,*}, Paul Tatner^a, Fran Stewart^a, Ryan Welton^b^a School of Engineering & Science, University of Paisley, Paisley PA1 2BE, United Kingdom^b Cobalt Development Institute 167 High Street, Guildford, GU1 3AJ, United Kingdom

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Abstract

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals and has diverse industrial importance. It is cycled in surface environments through many natural processes (*e.g.* volcanic eruptions, weathering) and can be introduced through numerous anthropogenic activities (*e.g.* burning of coal or oil, or the production of cobalt alloys). The environmental behaviour of cobalt in terrestrial environment is relatively poorly studied and in particular where Co is used in industrial processes, the baseline information to support wider and long-term environmental impacts is widely dispersed. To support the adoption of new EU regulations on the risk assessment of chemicals, we review here the various aspects of the environmental chemistry, fate and transport of Co across environmental interfaces and discuss the toxicology and potential for bio magnification and food chain accumulation.

The soil-to-plant transfer of Co appears to be viable route to expose lower trophic levels to biologically significant concentrations and Co is potentially accumulated in biomass and top soil. Evidence for further accumulation through soil-invertebrate transfer and to higher trophic levels is suggested by some studies but this is obscured by the relatively high variability of published transfer data. This variation is not due to one particular aspect of the transfer of Co in terrestrial environments. Influences are from the variability of geological sources within soil systems; the sensitivity of Co mobility to environmental factors (*e.g.* pH) and the variety of life strategies for metal elimination/use within biological species. Toxic effects of Co have been suggested for some soil–plant animal studies however, uncertainty in the extrapolation from laboratory to field is a major limitation.

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Keywords: Cobalt; Bioaccumulation; Secondary poisoning; Environmental variability; Bioavailability; Risk**Contents**

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1. Introduction

1.1. Industrial and domestic use

Cobalt has many strategic industrial uses in cutting tools, super alloys, surface coatings, high speed steels, cement carbides, diamond tooling, magnets, ceramics and pigments (CDI, 2006). It is the 31st most abundant element in the crust (Krauskopf & Bird, 1995) and is mined in 17 countries, the most significant deposits being associated with Ni/Cu production in Africa and from arsenide ores in Canada and Morocco. Deep sea nodules and crusts provide 2.5–10 million tonnes of reserves and currently (2007) globally production levels are ~54,000 tonnes/year (CDI, 2007).

The behaviour of Co in the environment has previously been reviewed (Hamilton, 1994) and with the increased capability of analytical techniques and improved understanding of metal behaviour in the environment (Hursthouse, 2001), it is timely to consider further developments, particularly in light of changes to the legislative environment.

Within the European Union this has recently become of more interest with the adoption of Regulation (EC) No 1907/2006 EU REACH legislation (Registration, Evaluation, Authorisation and restriction of Chemicals) requires producers to establish chemical safety assessments with the aim to ensure that potential hazards are both understood and suitably managed. This requires the holistic assessment of environmental fate and effects of substances (Huijbregts, 1999) and has also recently extended globally (e.g. the OECD's Strategic Approach to International Chemicals Management (SAICM) project, OECD, 2007).

Technical guidance (EC, 2003) has been provided to provide a generic approach to risk assessment, focussing on human health and the wider environment. Ecological testing being incorporated with environmental fate and dispersion data to demonstrate likely exposure based on predicted exposure concentration (PEC) and predicted no effect concentration (PNEC). This approach works well for some substances which are volatile and are liable to diffuse through the environment (e.g. persistent organic pollutants) and where bio-concentration, -accumulation and -magnification factors can be used to predict PEC_{oral} and compare to $PNEC_{oral}$ for wider risk assessment.

However, for the metallic elements, the situation is further complicated by the knowledge that biological availability, regulation and accumulation are metal and biological species-dependent (Gál et al., *in press*) and relationships are often non-linear. Similar tissue concentrations may be derived from very different exposure and accumulation conditions (Hendrickx et al, 2004). Recently, it has been shown that, for many naturally occurring elements (e.g. Cu, W), the data available to establish suitable assessment is lacking (Sadhra et al., 2007; Koutsospyros et al., 2006).

This review is based on the assessment of the terrestrial bioaccumulation and poisoning potential of Co and considers the key compartments of the assessment process highlighting data gaps and conflicts. A summary assessment framework or conceptual model is presented in the discussion section, highlighting the major areas of uncertainty.

1.2. Cobalt as an essential element

Cobalt is naturally occurring element and it is widely distributed in rocks, soils, water and vegetation. It is usually found in association with nickel. Cobalt occurs in two oxidation states (Co^{2+} and Co^{3+}). However, with the exception of certain complexes, Co^{3+} is thermodynamically unstable under typical redox and pH conditions (Nagpal, 2004; Palit et al., 1994).

Cobalt is essential in trace amounts for humans and other mammals as it is an integral component of the vitamin B₁₂ complex (Smith et al., 1981). This form of Co is obtained from microorganisms or from animal sources (USEPA, 2005). Vegetable sources of Co are important to ruminant animals (sheep and cattle). Cobalt deficiency in humans is similar to vitamin B₁₂ deficiency, with symptoms of anaemia and with problems of the nervous system. As little as 0.1 µm Co as vitamin B₁₂ per day is needed by adults, and total Co intake in the range 10 to 1800 µm per day (ATSDR, 2004) can be consumed on a daily basis without it being a hazard to human health (Atta-Aly, 2003). Cobalt in a different chemical form (i.e. not as part of vitamin B₁₂) will stimulate blood formation, but this is unlikely to be a normal action. Although its essentiality in higher, non-leguminous plants is not clearly proven, there is some evidence of a favourable effect

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