

# Direct and indirect effects of iron on river ecosystems

Kari-Matti Vuori

*Vuori, K., Department of Biology, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland*

*Received 3 March 1995, accepted 15 July 1995*

The direct and indirect effects of iron on the structure and function of lotic ecosystems are reviewed. In addition to the mining of Fe enriched ores, intensified forestry, peat production and agricultural draining have increased the load of iron in many river ecosystems. The effects of iron on aquatic animals and their habitats are mainly indirect, although the direct toxic effects of  $\text{Fe}^{2+}$  are also important in some lotic habitats receiving Fe-enriched effluents in cold seasons, in particular. Ferric hydroxide and Fe-humus precipitates, on both biological and other surfaces, indirectly effect lotic organisms by disturbing the normal metabolism and osmoregulation, and by changing the structure and quality of benthic habitats and food resources. The combined direct and indirect effects of iron contamination decrease the species diversity and abundance of periphyton, benthic invertebrates and fishes. Sorption and co-precipitation of metals by Fe-oxides decrease the bioavailability and toxicity of water-borne metals, but may increase the dietary supply of metals and lead to toxic effects along the food chain. At the cellular level, Fe functions both as a detoxification mechanism, as well as a cell degeneration agent by inducing the formation of hydroxyl free radicals. More research is needed on the factors that affect the environmental fate and ecotoxicological impacts of iron on river ecosystems. As the flux of iron is heavily affected by seasonally varying physical, chemical and biological processes, its impact on ecosystems should be studied on multiple spatial, and temporal scales and at different levels of biological organisation.

## 1. Introduction

Iron has an essential role as a constituent of enzymes, such as cytochromes and catalase, and of oxygen-transporting proteins, such as haemoglobin and myoglobin. In fresh waters, iron is also an important nutrient for algae and other organisms. Due to its high abundance within the earth's crust, iron is ubiquitous in all freshwater environments and often reaches significantly higher concentra-

tions in water and sediments than other trace metals (Livingstone 1963, Förstner & Wittmann 1979).

High iron concentrations in fresh waters have long been considered a problem. In domestic use, iron-enriched waters may induce rust formation on plumbing fixtures, the staining of laundry and a metallic taste in drinking water. Hence, much effort has been put into the retention of iron in drinking water (Theis & Singer 1974). The mining of iron-rich ores has caused the degradation of many river

ecosystems (e.g. Dahl 1963, Brown 1974, McKnight & Feder 1984, Boulton et al. 1994). More recently, intensified draining of peatlands, forests and arable lands, as well as dredging of iron-enriched river sediments, has increased the leaching of iron in many boreal river ecosystems (Heikurainen et al. 1978, Heikkinen 1990a, Ahtiainen 1992, Palko 1994, Vuori 1993, 1995).

In lentic ecosystems, the role of iron in element cycling and ecosystem functioning is relatively well established (e.g. Sulzberger et al. 1990, Balistrieri et al. 1992). There is increasing evidence that iron may have a crucial impact on the structure and function of river ecosystems, too. However, knowledge of the effects of iron at different levels of biological organization is scattered in biogeochemical, medical, physiological, toxicological, limnological and ecological literature. Hence, it is my aim to provide a short overview of the direct and indirect effects that iron may have on river ecosystems. In this context, I consider direct effects as those causing the impairment of animal survival, growth and reproduction due to toxic action of iron compounds, whereas indirect effects are those which somehow limit or enhance individual access to resources or the quality of those resources. Although I also consider some of the effects that iron has on plants, those will be considered mainly as indirect effects. More information on the impact of iron on freshwater and wetland plants is provided, for example, by Snowden and Wheeler (1993). While effects of iron on fish have been more extensively referred to in some earlier studies (for references, see Peuranen et al. 1994), I will pay more attention to the factors that affect the environmental fate and ecotoxicological effects of iron on lotic organisms and whole ecosystems. This review is not an exhaustive one, but rather aims to outline future needs for iron research in river ecosystems.

## 2. Speciation and concentration of iron in river waters

As with all trace elements, the spatio-temporal variability of iron concentrations and speciation of rivers is great, both at the macro and micro scale (Andelman 1973, Davison & DeVitre 1992, McKnight et al. 1992). Iron concentration and speciation in water depends on redox and light

conditions, pH, and the amount and type of dissolved organic matter. In non-humic circum-neutral rivers, Fe(II) is rapidly oxidized to insoluble Fe(III) oxyhydroxides. However, dissolved or colloidal organic material may stabilize Fe(II) and retard its oxidation (Theis & Singer 1974). Further, Fe(III) complexed with organic compounds can be readily photoreduced by UV light to the ferrous state (Francko & Heath 1982, Sulzberger et al. 1990), which may cause large diurnal fluctuations in the speciation and concentration of iron. Significant spatio-temporal fluctuations in the concentrations of Fe(II) and Fe(III) also take place due to changes in flow conditions, amount and type of dissolved organic matter, pH and redox conditions (Davison & DeVitre 1992, Calmano et al. 1993).

Oxidation of Fe(II) leads to the formation of amorphous Fe oxides. In the pH range of 5 to 8, this oxidation proceeds according to the rate law:

$$-d[\text{Fe(II)}]/dt = k[\text{Fe(II)}]\text{P}_{\text{O}_2}[\text{OH}^-]^2$$

The second-order dependence of the reaction on hydroxyl ions makes it very sensitive to pH. In aerobic soft waters of pH 8, 7, 6 and 5 at 10°C, the half-lives for the removal of Fe(II) are 2.34 min, 234 min, 390 h and 1625 days, respectively (Davison & DeVitre 1992). During the cold seasons, this implies that even at near circumneutral conditions, the Fe(II)-enriched drainage waters flushing into a stream may remain toxic for extended distances along it.

The oxidation of Fe(II) is accelerated by trace metals, phosphate, fluoride and particles, including autocatalysis by fresh Fe oxides. Micro-organisms, such as the bacteria *Thiobacillus ferrooxidans* greatly enhance Fe(II) oxidation in acid streams, in particular. The oxidation of Fe(II) may be inhibited for example, by tannic and humic acids, as well as sulfate, nitrate and chloride ions (Davison & DeVitre 1992).

Both non-reductive and reductive reactions may cause the dissolution of Fe(III) oxyhydroxides. In aquatic environments, reductive dissolution mechanisms are more important, whereas in soils, nonreductive dissolution may be important (Davison & DeVitre 1992). The role of bacteria and phytoplankton is also important because they may release such redox-active substances as organic acids, phenols, and humic- and-fulvic type acids. The biota maintain redox microenvironments, colonize

particles and induce aggregation. Reductive dissolution mechanisms in natural waters are still poorly understood, but the most important mechanisms of Fe(II) release include the reduction of Fe(III) hydroxides with dissolved sulfides and organic compounds, photo-induced dissolution, and reductive, enzymatic reactions on the surfaces of phytoplankton (Davison & DeVitre 1992).

The oxidized Fe particles in river water are removed by settling on the riverbed where they may be periodically resuspended, depending on their size and the velocity of the current. In reducing sediment layers, some of the Fe(III) oxyhydroxides are reduced to Fe(II). One part of this reduced Fe(II) diffuses upwards and is re-oxidized, while the other part is removed by the formation of authigenic minerals such as siderite, vivianite or iron sulfide (Davison & DeVitre 1992).

In most river waters, iron is predominantly transported in the particulate fraction (Förstner & Wittmann 1979, Burman 1983, Johnson & Thornton 1987, Davison & DeVitre 1992). The ratio of particulate to dissolved Fe in the world's rivers is approximately 500:1. However, as the dissolved fraction frequently contains colloidal particles, this ratio is arbitrary (Davison & DeVitre 1992). More notably, in many boreal humic rivers, iron is carried into them as colloidal Fe-humus complexes derived from the peatlands of the catchment area (Heikkinen 1990a). Livingstone (1963) estimated the global average of iron in river water to be  $670 \mu\text{g} \times \text{l}^{-1}$ , but Förstner and Wittmann (1979) considered that truly dissolved values might be as low as  $0.7\text{--}6.6 \mu\text{g} \times \text{l}^{-1}$ . However, much higher

concentrations have been observed in many boreal rivers, with drainage from peatlands (Heikkinen 1990a), acid mine, (e.g. Johnson & Thornton 1987, Boulton et al. 1994) and sulphate soils (Vuori 1995). The highest dissolved iron concentrations have been measured in acid, nonhumic rivers contaminated by mine drainages (Table 1).

In general, dissolved iron is defined as the Fe analysed in the filtrates after passage of the water through a membrane pore size of approximately  $0.5 \mu\text{m}$  in diameter. However, even these filtrates may contain iron associated with fine colloidal particles (Cameron & Liss 1984). Cameron and Liss (1984) pointed out that there is a drastic difference between expected and measured concentrations of dissolved iron in river waters. This contradiction is partly explained by organic iron complexes, but the majority of the "excess" iron is in the form of colloidal particles. In the presence of dissolved organic matter, this colloidal iron is stabilized, which explains the high realized iron concentrations in most rivers, and in humic rivers, in particular. Due to the photoreduction of Fe hydroxides, a great deal of variation in Fe concentrations may occur, particularly in the summer (e.g. Francko & Heath 1982, Collienne 1983, McKnight et al. 1992).

Observations on the relationship between discharge and iron concentrations in the river water are contradictory. While some results display a strong, positive correlation of these two variables (e.g. Grieve 1984, Johnson & Thornton 1987), some show significant negative correlations (Wartiovaara 1978, Heikkinen 1990c). Large fluctuations in the fluxes and concentrations of iron in river water

Table 1. Examples of the annual means of total and dissolved Fe concentrations in river water. Mesh size of the filter in the parentheses.

River	Source of Fe	Total Fe $\text{mg} \times \text{l}^{-1}$	Dissolved Fe	Authors
Afon Coch	Acid mine drainage	194.7	$193.2(0.45 \mu\text{m} \times \text{l}^{-1})$	Boulton et al. 1994
River Vidaa	Mining and farming	31.8	$26.8(0.45 \mu\text{m} \times \text{l}^{-1})$	Rasmussen & Lindegaard 1988
River Kiiminkijoki	Diffuse (humus)	1.8	$1.3(1.2 \mu\text{m} \times \text{l}^{-1})$	Heikkinen 1990b
Keihäsoja Brook	Peat mining	2.7	$2.1(1.2 \mu\text{m} \times \text{l}^{-1})$	Heikkinen 1990b
Peat mine ditch	Drainage	4.5	$2.8(1.2 \mu\text{m} \times \text{l}^{-1})$	Heikkinen 1990b
Kalix River	Diffuse	0.7	$0.25(0.45 \mu\text{m} \times \text{l}^{-1})$	Burman 1983
Zambezi River	Diffuse	0.1		Hall et al. 1977
Luangwa River	Diffuse	0.2		Hall et al. 1977
River Kyrönjoki	Acid sulphate soils	1.8	$1.1(0.45 \mu\text{m} \times \text{l}^{-1})$	Vuori 1995
River Lehmäjoki	Acid sulphate soils	2.5	$1.6(0.45 \mu\text{m} \times \text{l}^{-1})$	Vuori 1995

occur particularly during storms and rapid floods (Johnson & Thornton 1987). During such floods, a larger proportion of stream flow is derived from surface run-off. Hence, the qualitative and quantitative properties of this surface run-off is likely to be of great importance in the concentrations of iron during floods.

Johnson and Thornton (1978) emphasized that iron concentrations in the Carnon River were dependent upon two seasonally controlled factors: a) the relative proportions of underground mine and surface, waters and b) the proportion of water infiltrating from the surface. In their study, a three to fourfold increase in Fe concentrations occurred with the onset of autumnal rainfall. This was largely due to the increase in the proportion of contaminated, infiltrated surface waters.

Heikkinen (1990c) reported a significant negative correlation between iron concentrations and discharge. The decrease in iron concentrations was particularly rapid at the rise of the spring flood when pH values decreased. Grieve (1984) observed, in hourly sampled data, a lag in iron concentrations after the flood peak. As with the data of Johnson and Thornton (1987), Heikkinen (1990c) attributed the increase in iron concentrations to the increase in the relative proportion of iron-rich runoff. In her study, however, the higher iron concentrations were observed during summer minimum discharges when a larger proportion of inflowing water was suggested to have come from deep, partly anaerobic

peat horizons enriched with iron. In contrast to the results of Heikkinen (1990c), Grieve (1984) suggested that the flood induced the flushing of dissolved organic matter into the river and, consequently, increased iron concentrations in the water.

In summary, because the mobilization and transport of iron in rivers is largely controlled by water-soluble organic complexing agents, the iron dynamics are determined by the same factors that cause changes in the quality and quantity of organic material transported in the river. In order to understand the iron dynamics of a river, it is necessary to know what kind of organic material, when and to what extent it is flushed into the river, and the effect of different biotic and abiotic factors on the fate of the iron complexed with this material.

### 3. Uptake and direct toxic effects of iron in aquatic animals

Uptake of Fe into aquatic animals occurs from two sources: food and water. The interchange between the two oxidation states of Fe has great influence on the relative proportion of these uptake routes. Dissolved Fe(II) and other metals are taken predominantly via water, whereas Fe(III) precipitates may significantly contribute to the dietary Fe concentrations of aquatic animals. Within the animals, Fe is actively transported across membranes by endocytosis (Luoma 1983, Simkiss & Taylor 1989). Fe-

Table 2. Estimates of the acute and chronic toxicity of Fe to aquatic invertebrates.

Species	Measure of toxicity	Fe mg × l <sup>-1</sup>	Authors
<i>Daphnia magna</i>	LC <sub>50</sub> 48 h	5.9	Biesinger & Christensen 1972
<i>Daphnia magna</i>	EC <sub>50</sub> 21 a (reproduction)	5.2	Biesinger & Christensen 1972
<i>Daphnia magna</i>	LOEC 21 a (reproduction)	4.4	Biesinger & Christensen 1972
<i>Asellus aquaticus</i>	LC <sub>50</sub> 48 h Fe(III)	81.1	Furmańska 1979
<i>Asellus aquaticus</i>	LC <sub>50</sub> 48 h Fe(III)	183.0	Martin & Holdich 1986
<i>Asellus aquaticus</i>	LC <sub>50</sub> 96 h Fe(III)	124.0	Martin & Holdich 1986
<i>Asellus aquaticus</i>	LC <sub>50</sub> 62 h Fe(II)	3.0	Walter 1966
<i>Asellus aquaticus</i>	LC <sub>50</sub> 62 h Fe(II)	200–400	Maltby et al. 1987
<i>Leptophlebia marginata</i>	LC <sub>50</sub> 24 a	73.1	Gerhardt 1995
<i>Leptophlebia marginata</i>	EC <sub>50</sub> 120 h (feeding activity)	8.5	Gerhardt 1995
<i>Leptophlebia marginata</i>	EC <sub>50</sub> 24 a (feeding activity)	50.1	Gerhardt 1995
<i>Leptophlebia marginata</i>	EC <sub>50</sub> 120 h (escape behaviour)	19.8	Gerhardt 1995
<i>Leptophlebia marginata</i>	EC <sub>50</sub> 24 (escape behaviour)	23.5	Gerhardt 1995

enriched food may reduce the uptake of Fe via the gut membranes by inducing formation of thick Fe-hydroxide encrustations on the gut walls (Gerhardt 1995). Gerhardt (1995) only found Fe(II) occurring internally, in the eyes and trachea of the mayfly *Leptophlebia marginata*, whereas both Fe(II) and Fe(III) were found externally, on the body, gill and gut surfaces. Gerhardt and Westermann (1995) found a significantly higher uptake of Fe in the *Leptophlebia marginata* nymphs of a humic river, compared with a clearwater river. This was presumably due to the impact of humic material and microbial activity on the speciation of Fe.

Information on the toxicity of iron to aquatic animals is scarce and somewhat contradictory (Table 2). Further, most laboratory bioassays have not separated the impact of dissolved Fe(II) and Fe particles. Fe(II) is considered to be more toxic to aquatic animals than Fe(III) (Gerhardt 1992). In many toxicity tests, the acidification of the test solution via the formation of ferric oxyhydroxide, after the addition of iron as chloride or sulphide, may have also contributed to the observed toxic effects on aquatic organisms (Dave 1985). In general, the toxicity of iron seems to be highest in acid conditions where Fe(II) predominates (Gerhardt 1992).

Acutely toxic concentrations of iron in the laboratory exposures of invertebrates usually vary between 3 and 400 mg, even within the same species (Table 2). An exceptionally low 4 d LC<sub>50</sub> value of 0.32 mgFe × l<sup>-1</sup> was reported for *Ephemerebella subvaria* by Warnick and Bell (1969). The US EPA water quality criteria for freshwater aquatic life is 1.0 mgFe × l<sup>-1</sup>. This is principally derived from field observations of the adverse effects of iron. Obviously, factors affecting the concentration and speciation of iron greatly contribute to the variation in estimated iron toxicity (Dave 1984, Maltby et al. 1987).

Peuranen et al. (1994) observed damage in the gills of one-summer-old brown trout exposed to Fe(II) and Fe(III) at pH 5 and 6, with and without humic material. The nominal total iron concentration of the exposure water was 2 mg × l<sup>-1</sup>. Staining of whole gill arches indicated that at least some of the Fe was bound to the gills even in the presence of humic material. Gill damage, consisting of fusion of the lamellae and hypertrophy of the epithelial

cells, induced reduced oxygen uptake and impairment of the ion regulation of the Fe-exposed brown trout. The gill damage was more adverse at pH 5 than at pH 6 (Peuranen et al. 1994). Although not clearly distinguished as such, the results of Peuranen et al. (1994) reveal the combined effects of Fe accumulated within, and precipitated on the gills. The indirect effects of Fe precipitates are reviewed in Chapter 4.

A potential mechanism of iron toxicity includes its role in DNA and membrane damage. Vertebrate studies have shown that high cellular concentrations of iron, ferrous iron in particular, may cause cell degeneration. The mechanism of this process is not fully understood, but it includes the iron-catalysed auto-oxidation of dopamine, which in turn generates hydroxyl-free radicals. Together with oxygen, these free radicals are highly reactive and may cause site-specific oxidative damage when produced in excess. Excessive production of free radicals in tissues may be caused by increased free iron concentrations following, for example, haemorrhage or disorder in the iron metabolism (e.g. Halliwell & Gutteridge 1984, Fornstedt et al. 1990, Stevens & Kalkwarf 1990, Obata et al. 1993). Iron-enriched food may also cause elevated Fe levels in tissues (Jones et al. 1981, Luoma 1983).

In most laboratory bioassays, the toxicity of iron to aquatic animals has been attributed to the motion inhibiting or smothering effects of Fe-hydroxide or Fe-humic precipitates on gills, eggs or other surfaces. As these kinds of toxic actions limit an individual's access to essential resources, such as oxygen or food, they are considered here as indirect effects.

## 4. Indirect effects of iron on aquatic animals and their resources

### 4.1. Iron as a physical stressor

Formation of iron precipitates on biological surfaces has frequently been reported to effect the survival, reproduction and behaviour of aquatic animals (e.g. Walter 1966, Smith et al. 1973, Smith & Sykora 1976, Amelung 1982, Gerhardt 1992). Von Lukowicz (1976) concluded that the toxic effect of iron on rainbow trout, at neutral pH, was due to the

precipitation of ochre (ferric hydroxide) on the egg and gill surfaces. Field observations on the clogging of fish gills by Fe-hydroxide precipitates in Fe-contaminated rivers are frequent (e.g. Andersson & Nyberg, 1984, Weatherley et al. 1991, Steffens et al. 1992). The indirect effects of Fe-hydroxide suspension on fishes may also include behavioural avoidance (Updegraff & Sykora 1976). Smith et al. (1973) suggested that a decreasing hatching success for fathead minnow, with decreasing iron concentrations, was due to the greater amount of small ferric-hydroxide particles at low Fe concentrations. These small particles were suggested to induce suffocation via clogging of the egg pores. Amelung (1982) suggested that the increased mortality of rainbow trout eggs, exposed to Fe(II), was due to the formation of thick ironhydroxide layers on the egg surfaces.

In addition to the Fe hydroxides, other Fe precipitates may cause physical stress. Gerhardt (1992) described how benthic invertebrates used their mouth parts in trying to move Fe-humus precipitates from their surfaces. Gerhardt also observed Fe precipitates on the thorax and gills of Ephemeropteran larvae, reared in the laboratory at low pH and exposed to high Fe concentrations. Wellnitz et al. (1994) demonstrated behavioural avoidance of Fe/Mn-bacteria precipitates in Ephemeroptera, Plecoptera and Trichoptera species, and attributed the high mortality of Ephemeroptera, in particular, to the smothering effect of these precipitates. Further, Vuori (1995) suggested that amorphous Fe-humus precipitates on the tracheal gills contributed to the high mortality of translocated hypsychid caddis larvae in humic rivers loaded by runoff from acid sulphate soils.

More notably, iron-hydroxide precipitates may drastically alter the physical characteristics and quality of benthic habitats. Formation of such hydroxide precipitates is characteristic for rivers receiving iron-rich runoff from acid sulphate soils disturbed by mining activities (e.g. Dahl 1963, Scullion & Edwards 1980, McKnight & Feder 1984, McKnight et al. 1992, Boulton et al. 1994) or agricultural drainings (Rasmussen & Lindegaard 1988, Vuori 1993). Furthermore, iron input from groundwater may also induce Fe-hydroxide precipitation (Amelung 1982, Wellnitz et al. 1994).

In an acid river, with extremely high iron concentrations (up to  $260 \text{ mg} \times \text{l}^{-1}$ ), the neutralizing

effect of a tributary induced the precipitation of ferrihydrite and co-precipitation of other metals (Boulton et al. 1994). These precipitates formed an obvious orange blanket over the streambed and, according to the authors, acted as a sink of metals. Boulton et al. (1994) did not specify the composition of this blanket, but Wellnitz et al. (1994) described a similar kind of ochre-coloured, gelatinous coating in association with blooms of iron-depositing bacteria. A detailed review of the physical and chemical characterization of iron particles and precipitates occurring in fresh water is provided by Davison and DeVitre (1992).

These kinds of precipitates have been observed to restrict the distribution, abundance and diversity of fishes (Dahl 1963, Amelung 1982), benthic invertebrates (e.g. Thorup 1966, Parsons 1968, Hynes 1970, Letterman & Mitsch 1978, Scullion & Edwards 1980, McKnight & Feder 1984, Rasmussen & Lindegaard 1988, Gower et al. 1994, Gerhardt & Westermann 1995) and periphyton (McKnight & Feder 1984, Sheldon & Skelly 1990, Gower et al. 1994) in streams. Often, iron is the main, but not sole component of such precipitates (Davison & DeVitre 1992). For example, McKnight and Feder (1984) observed a rapid formation of Fe- and Al-hydroxide precipitates on the colonization substrates and, consequently, a drastic decline in both the abundance and diversity of periphyton in an acid stream loaded with mine drainages. The abundance and species richness of benthic invertebrates declined in the areas where pH increased above 5.0 and metal precipitates covered the streambed. Sheldon and Skelly (1990) demonstrated that Fe/Mn oxides and associated *Leptothrix ochracea* bacteria displaced the algal community and covered substrates with an ochre-coloured layer 1–4 mm thick.

Rasmussen and Lindegaard (1988) studied macroinvertebrates in several circumneutral streams loaded differently by iron-rich drainage from arable lands. They found a significant decrease in species number and abundances with increasing amounts of dissolved iron. At lower Fe concentrations, the authors attributed adverse effects to Fe-precipitates limiting food resources and destabilizing substrates. At higher Fe levels, the combined effects of precipitates and toxic Fe(II) were suggested to contribute to the drastic decrease in benthic diversity and abundance.

The results of Rasmussen and Lindegaard (1988) imply that the same invertebrates that tolerate eutrophication are also tolerant of Fe pollution. However, contrary to the eutrophicated rivers, where population densities are often high, the iron-polluted streams had very low population densities with a view tolerant species. In their data, the first invertebrates eliminated by increasing Fe concentrations (between  $0.20$  and  $0.25 \text{ mgFe}^{2+} \times \text{l}^{-1}$ ) were grazers feeding on periphyton and other biofilm. Up to concentrations of  $10$  and  $30 \text{ mgFe}^{2+} \times \text{l}^{-1}$ , only ten and seven taxa persisted, respectively. The latter group included Tubificidae, Chironomidae (*Macropelopia nebulosa*, *Prodiamesa olivacea* and *Chironomus thummi* group), *Lymnaea peregra*, *Sialis lutaria* and *Nemoura cinerea* (found in up to  $11 \text{ mgFe(II)} \times \text{l}^{-1}$ ).

Also Wellnitz et al. (1994) suggested that the combined direct toxic and indirect physical effects of high iron and manganese concentrations, and associated blooms of ferromanganese-depositing bacteria *Leptothrix ochracea*, resulted in low diversity and density of lotic invertebrates and diatoms.

In addition to the descriptive study, Wellnitz et al. (1994) also verified their hypotheses by habitat choice, feeding and *in situ*-exposure experiments. The blooms of *Leptothrix ochracea*, which become encrusted with iron and manganese oxides, formed extensive, ochre-coloured, gelatinous coatings on the stream substrates in the summer. Later in the autumn and winter, when Fe and Mn concentrations decreased and the blooms disappeared, benthic diversity and abundance recovered to equal levels with those of reference stations. Five of the tested species preferred substrates free of Fe/Mn oxides and bacteria, two did not show any preference and one preferred the bacterial deposits. Of the nine species exposed to the precipitates, only three Ephemeroptera suffered significantly higher mortality compared with the controls. However, the *in situ* exposures did not distinguish between direct metal toxicity, the smothering effect of the bloom or some other, indirect factor.

As the metal-bacteria deposits encrusted the mayfly gills and clogged the labial palps, appearing to hamper their motion, it seems plausible to presume that indirect effects on respiration and/or feeding ability may have been of greater im-

portance than the direct toxic action of metals or bacteria (Wellnitz et al. 1994, see also Gerhardt 1992). In feeding experiments, metal-bacteria coatings proved to be inadequate food for most of the tested species. Hence, species, specific differences in the habitat and food preferences, and tolerance against Fe/Mn-bacteria precipitates, all seemed to contribute to the drastic decrease in benthic diversity, density and distribution (Wellnitz et al. 1994).

#### 4.2. Impact of iron on the uptake and effect of contaminants

The dissolution/precipitation dynamics of Fe play an important role in the fate, bioavailability and toxic effects of trace metals and organic toxicants.

Fe(II) ions promote photodecomposition of organic contaminants, such as chlorophenols, in acidic conditions. The major agent responsible for this decomposition is believed to be hydroxyl radicals formed by the photochemical dissociation of the Fe(III)-hydroxy complex (Kawaguchi & Inagaki 1994).

The sorption and coprecipitation of metals by Fe-oxides is an important mechanism, decreasing bioavailability and the toxic effects of metals in aerobic, Fe-enriched freshwater, in particular (e.g. Johnson & Thornton 1987, Calmano et al. 1993, Boulton et al. 1994). For example, Boulton et al. (1994) reported extremely high dissolved Mn, Cu, Zn, Al, and especially Fe concentrations (up to  $260 \text{ mgFe} \times \text{l}^{-1}$ ) in the highly acidic river Afton Goch polluted by mine drainages. Further downstream, the neutralizing effect of a tributary induced an effective adsorption of other metals by the ferrihydrate precipitates. Gerhardt (1995) suggested that coprecipitation of Cd with Fe ameliorated the Cd-induced ion balance disturbance in *Leptophlebia marginata* nymphs.

It is the oxidation of Fe(II), and a consequent formation of  $\text{Fe(OH)}_3$ , that produces hydrogen ions and contributes to the acidification and increased solubility of other metals in soft water streams in particular (Amelung 1982, Calmano et al. 1993). Hence, Fe pollution in a stream often creates longitudinal zones with different speciation in Fe and, consequently, varying ecotoxicological effects. The first impact zone is with a low pH and high concen-

trations of dissolved Fe and other metals, and subsequent direct toxic effects on biota. Further downstream, often after neutralization of the water, a second zone follows. Here particulate Fe oxyhydroxides coprecipitate with other metals and organic material and, induce physical stress on the biota.

Iron-oxide precipitates on the exoskeleton of aquatic insects may increase the larval whole-body metal concentrations (Hare 1992, Vuori 1993), as well as metal concentrations of aquatic macrophytes (Dietz 1973, Vuori in prep.). Burrowing invertebrate species, in particular, or those that otherwise live in close contact with sediments, tend to have heavy depositions of iron oxides on their body surfaces. Consequently, larval concentrations of metals strongly absorbed onto iron oxides, such as Pb and As, may increase with an increasing formation of these iron encrustations (Hare 1992). A similar correlation has been observed for aquatic bryophytes (Vuori in prep.).

Such scavenging of metals by iron oxides may have indirect effects on predators or herbivores consuming invertebrates or macrophytes enriched with iron. These indirect effects may include the increased accumulation of metals via the contaminated food (Patrick & Loutit 1978, Dallinger et al. 1987) and the consequent toxic effects on predators (Handy 1993). The excess dietary iron concentrations have been related to the disturbed haem synthesis in mice exposed to 2,3,7,8-tetrachlorodibenzo-(p)-dioxin (Jones et al. 1981).

Iron-enriched food itself may also have deleterious effects on aquatic invertebrates. The elevated dietary Fe supply may increase cellular Fe concentrations (Jones et al. 1981, Luoma 1983). This may, in turn, increase production of free radicals and cause oxidative cellular damage (Obata et al. 1993). Further, Gerhardt (1992) described constipation in *Leptophlebia marginata* mayfly nymphs fed with iron-enriched detritus in acid (pH 4.5) conditions. This constipation may have occurred because of Fe-induced ulceration of the gut membrane, formation of precipitates preventing absorption of food, inhibition of normal muscular function or the dehydration and hardening of the food (Gerhardt 1992). Gerhardt (1995) found that Fe-induced constipation decreased the food consumption of the *Leptophlebia marginata* nymphs. However, the

iron concentrations used in these studies were very high ( $4\text{--}50\text{ mgFe} \times \text{l}^{-1}$ ).

Still, it is likely that even at more relevant concentrations, iron precipitates on animal and plant surfaces may cause qualitative and quantitative changes in food resources, and animal feeding behaviour. Maltby and Crane (1994) observed a significant decrease in the feeding rate of *Gammarus pulex* exposed to metalliferous effluents in the West Okement River (Fe concentrations  $0.32\text{--}2.34\text{ mg} \times \text{l}^{-1}$ ). The iron residues in the gammarids and laboratory toxicity tests confirmed that Fe was the major toxicant inducing a decreased feeding rate. Both in the field and laboratory experiments, the leaf material used as a food source had considerably greater metal concentrations than the ambient water. Hence, it is plausible to presume that Fe-enriched food significantly contributed to the gammariid feeding behaviour.

Further, Vuori (in prep.) measured average concentrations of up to  $56\text{ mgFe} \times \text{g}^{-1}$  (dry weight) in the bryophyte *Fontinalis dalecarlica* in the rivers which had iron concentrations ranging between 1.0 and  $3.0\text{ mgFe} \times \text{l}^{-1}$ . The high iron concentrations in mosses were attributed to the heavy encrustations of metal oxides on the outer leaf surfaces. Concomitantly with the iron encrustations, the moss-dwelling isopod *Asellus aquaticus* exhibited a significant decrease in the relative proportion of *Fontinalis* leaves in its gut content. This was suggested to be due to the poor nutritional value of these encrusted leaves (Vuori in prep.). These kinds of indirect effects of iron on the structure and function of the lotic food webs are an important area for further research.

At the cellular level, Fe also functions as a detoxification agent. Ferritin, an iron storage protein in the intestinal mucosal cells of animals, strongly adsorbs Cd. This is considered the main reason why iron deficiency increases adsorption of dietary cadmium (Flanagan et al. 1978, Jonnalagadda & Prasada Rao 1993). In the soft tissues of decapod crustaceans, Fe granules are considered to function both as storage for physiological requirements, and in detoxification or removal of surplus metals (Gibson & Barker 1979, Vogt & Qunitio 1994). Further, the iron-rich pigment, haemoglobin, has been suggested to play an important role in the detoxification



processes of *Chironomus* (Osmulski & Leyko 1986).

### 4.3. Impacts of iron on the availability of nutrients and light

The availability of Fe itself as a nutrient depends on the rate of Fe(II) oxidation and the stability of the resultant Fe(III). In circumneutral clear water, under oxygen-rich conditions, Fe(II) may be rapidly oxidized to insoluble Fe(III) hydroxides and oxides, which limits Fe availability for the primary producers. However, dissolved organic material, a low pH and cold temperatures may retard the oxidation of Fe(II). The stabilization by humic substances increases the bioavailability of Fe (Theis & Singer 1974). Cameron and Liss (1984) attributed this Fe stabilization to the surface uptake of Fe(II) by humic and tannic acids, detergents and the inorganic anions silicate and especially phosphate. However, some diatoms may accumulate Fe from solutions containing complexed Fe(III) by utilizing kinetic differences in the dissociation of complexed Fe and Fe oxide (Luoma 1983).

Iron, especially in association with humic substances, is involved in several aspects of phosphorus dynamics in fresh waters. Fe(III) hydroxides and oxides readily adsorb and precipitate phosphate. However, the presence of humic substances has been frequently observed to maintain a pool of both dissolved Fe and phosphate (Koenings & Hooper 1976, Francko & Heath 1982, De Haan et al. 1990). In aerobic conditions, the interaction between colloidal organic matter and Fe has been observed to decrease phosphate adsorption onto Fe-organic complexes and increase P availability for phytoplankton (Koenings & Hooper 1976). Phosphorus binding occurred when Fe was present as Fe(III), whereas ferrous iron-humic complexes could not bind P. Hence, it has been suggested that humic substances increase bioavailability of both iron and phosphorus by retarding the oxidation of Fe(II) (Theis & Singer 1974, Koenings & Hooper 1976, De Haan et al. 1990). However, Giesy (1976) demonstrated that humic acids stimulated growth of Fe-starved *Scenedesmus obliquus* cells, both in the presence and absence of EDTA, indicating

that under Fe-limiting conditions humic acids do not create a soluble Fe pool but rather act as an Fe-sparing factor.

Iron is suggested to contribute strongly to colour formation in humic rivers (Heikkinen 1990c). Heikkinen (1990c) reported a clear seasonal variation in the colour-producing properties of the dissolved organic matter, which she attributed partly to changes in the iron content. This may be because Fe(III) hydroxide, a dominant form of Fe in aerobic conditions, has charge-transfer bands in the ultraviolet light region, which have tails coming into the visible region (Cotton & Wilkinson 1980, Heikkinen 1990b). Otto and Svensson (1983) observed that only light of longer wavelength (640 nm) reached the bottom of a humic river. As benthic algae have maximum light adsorption at 405 and 640 nm wavelengths, the staining of Fe-complexed humic substances may significantly decrease the autochthonous energy supply of the humic rivers. Hence, one important indirect effect of iron on humic river ecosystems, in particular, may be its effect on light conditions, and consequent impact on primary production and species interactions affected by the quality and quantity of light.

### 5. Outline of future needs for iron research in river ecosystems

Recent research results show that problems with Fe load from mine fields prevail decades after the abandonment of the mines (e.g. McKnight et al. 1992, Boulton et al. 1994, Gower et al. 1994). These results should be warning signals: whenever human activities disturb the balance of soils enriched with iron and other metals, problems are likely to arise.

In natural watersheds, weathering processes are responsible for the transfer of iron to rivers. These weathering processes involve the dissolution of Fe(II), but when transported into an oxidized soil layer, the ferrous iron is rapidly oxidized in neutral conditions to insoluble oxyhydroxides. In soils, the oxidized Fe is stabilized as small colloidal particles by humic substances. In natural conditions, transfer of this fraction to river ecosystems occurs slowly, mainly via physical erosion processes (Davison & DeVitre 1992). However, intensifying land-use has

changed the flux of iron to the rivers in multiple ways. Many limnological studies have demonstrated the close association between land-use and the increasing load of iron, nutrients, humus and suspended solids to streams and rivers (e.g. Hartikainen & Ylihalla 1986, Heikkinen 1990a, Ahtiainen 1992). Hence, concomitantly with the increased diffuse load of nutrients to aquatic ecosystems, iron load has also increased. Although an increasing number of lotic ecosystems clearly have a combined problem of iron, nutrient and humus load, our knowledge of the interaction, fate and ecological effects of these substances on river ecosystems is still poor.

In Scandinavia, forest ditching has changed the hydrology and water quality of many streams more than any other single factor. Often a drastic increase in the iron concentrations of the receiving streams and rivers is one of the main changes that ditching induces in the water quality (Heikurainen et al. 1978, Bergquist et al. 1984, Ahtiainen 1992). Similarly, peat production activities have significantly increased the leaching of iron to many stream and river ecosystems (Heikkinen 1990ab). Further, ditching of iron-enriched arable lands contributes greatly to the increasing iron concentrations in many rivers. The intensified use of subsurface drainage pipes increases the acidification of rivers by directly carrying Fe(II) from the soil horizon to the watercourse, from acid sulphate soils in particular (Palko 1994). In addition to the ditching of the terrestrial habitats of the watershed, river restructuring and the digging of iron-enriched sediments and riverbanks may significantly increase the leaching of iron and other metals into the rivers (Calmano et al. 1993).

These different land-use activities often cumulatively increase iron concentrations from headwaters to estuaries. Headwaters are more affected by forestry and peat mining, whereas agricultural draining and the restructuring of a river for regulation and flood control purposes are of more importance in the mid and downstream reaches (Hildén & Rapport 1994). In association with the draining and restructuring works, naturally-filtering riffle habitats are often cleared. This physical changing of the streambed may significantly enhance the transportation of particulate matter and associated metals downstream (Gore 1985).

Cold climates may further increase leaching of Fe(II) from acid, Fe-enriched soils and sediments

because the microbial oxidation of Fe(II) is significantly retarded (Hartikainen & Yli-Halla 1986). Due to the long half-lives in the removal of Fe(II), it may also be transported long distances before oxidation to Fe(III), in cold and acid conditions in particular (Davison & DeVitre 1992). Hence, many Nordic streams and rivers may be more susceptible to the direct and indirect effects of iron than rivers in warmer climates. More knowledge on the toxicity of iron is needed, especially at low temperatures.

In summary, an increasing load of iron may significantly change both the structure and function of lotic ecosystems. In order to effectively protect river ecosystems, more research is needed on the factors that affect the environmental fate and ecotoxicological effects of iron on river ecosystems. In natural systems, iron continuously fluxes through both physical (sedimentation, eddy diffusion, bioturbation) and chemical (reduction, oxidation) processes (Davison & DeVitre 1992). This implies that the relative importance and intensity of the direct and indirect effects of iron are likely to vary both according to the time, place and covarying ecological processes. Hence, future studies on the ecotoxicological effects of iron should deal simultaneously with different spatial and temporal scales along the river continuum, as well as with different levels of biological organization.

*Acknowledgements.* This study is a contribution of the Graduate Programme of Ecotoxicology established by the Academy of Finland. Comments by Almut Gerhardt, Jussi Kukkonen and Pekka Vuorinen improved the paper and are gratefully acknowledged.

## References

- Ahtiainen, M. 1992: The effects of forest clear-cutting and scarification on the water quality of small brooks. — *Hydrobiologia* 243/244: 465–473.
- Amelung, M. 1982: Auswirkungen gelöster Eisenverbindungen auf die Ei- und Larvalentwicklung von *Salmo gairdneri* (Richardson). — *Arch. Fischwiss.* 32: 77–87.
- Andelman, J. B. 1973: Incidence, variability and controlling factors for trace elements in natural, fresh waters. — In: Singer, P. C. (ed.), *Trace metals and metal-organic interactions in natural waters*: 57–88.
- Andersson, P. & Nyberg, P. 1984: Experiments with brown trout (*Salmo trutta* L.) during spring in mountain streams at low pH and elevated levels of iron, manga-

- nese and aluminium. — Rep. Inst. Freshw. Res. Drottningholm 61: 34–47.
- Balistrieri, L. S., Murray, J. W. & Paul, B. 1992: The cycling of iron and manganese in the water column of Lake Sammamish, Washington. — *Limnol. Oceanogr.* 37: 510–528.
- Bergquist, B., Lundin, L. & Andersson, A. 1984: Hydrologiska och limnologiska konsekvenser av skogs- och myrdikning. — Uppsala Univ. Limnologiska Inst., Forskningsrapport Nr. 9, LIU 1984 B:4, Uppsala. 95 pp.
- Biesinger, K. E. & Christensen, G. M. 1972: Effects of various metals on survival, growth, reproduction and metabolism of *Daphnia magna*. — *J. Fish. Res. Board Canada* 29: 1691–1700.
- Boult, S., Collins, D. N., White, K. N. & Curtis, C. D. 1994: Metal transport in a stream polluted by acid mine drainage of the Afon Goch, Anglesey, UK. — *Environ. Pollut.* 84: 279–284.
- Brown, B. E. 1974: Effects of mine drainage on the river Hayle, Cornwall. A) Factors affecting concentrations of copper, zinc and iron in water, sediments and dominant invertebrate fauna. — *Hydrobiologia* 52:221–233.
- Burman, J.-O. 1983: Element transports in suspended and dissolved phases in the Kalix River. — In: Hallberg, R. (ed.), *Environmental biogeochemistry*. Proc. 5th Int. Symp. Env. Biogeochemistry (ISEB2), Ecol. Bull. (Stockholm) 35: 99–113.
- Calmano, W., Hong, J. & Förstner, U. 1993: Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. — *Wat. Sci. Tech.* 28: 223–235.
- Cameron, A. J. & Liss, P. S. 1984: The stabilization of “dissolved” iron in freshwaters. — *Water Res.* 18: 179–185.
- Collienne, R. H. 1983: Photoreduction of iron in the epilimnion of acidic lakes. — *Limnol. Oceanogr.* 28: 83–100.
- Cotton, F. A. & Wilkinson, G. 1980: *Advanced inorganic chemistry*. — John Wiley & Sons, New York. 758 pp.
- Dahl, J. 1963: Transformations of iron and sulphur compounds in soil and its relation to Danish inland fisheries. — *Trans. Am. Fish. Soc.* 92: 260–264.
- Dallinger, R., Prosi, F., Segner, H. & Back, H. 1987: Contaminated food and uptake of heavy metals by fish: a review and a proposal for further research. — *Oecologia* 73: 91–98.
- Dave, G. 1984: Effects of waterborne iron on growth, reproduction, survival and haemoglobin in *Daphnia magna*. — *Comp. Biochem. Physiol.* 78C: 433–438.
- Dave, G. 1985: The influence of pH on the toxicity of aluminium, cadmium and iron to eggs and larvae of the zebrafish, *Brachydanio rerio*. — *Ecotoxicol. Environ. Safety* 10: 253–267.
- Davison, W. & DeVitre, R. 1992: Iron particles in freshwater. In: Buffle, J. & Leeuwen van, H. P. (eds.), *Environmental particles Vol 1., Environmental analytical and physical chemistry series*, 1 ed.: 315–355.
- De Haan, H., Jones, R. I. & Salonen, K. 1990: Abiotic transformations of iron and phosphate in humic lake water revealed by double-isotope labeling and gel filtration. — *Limnol. Oceanogr.* 35: 491–497.
- Dietz, F. 1973: The enrichment of heavy metals in submerged plants. — In: Jenkins, S. H. (ed.), *Advances in water pollution research*, Proceedings of the 6th International Conference held in Jerusalem, June 18–23 1972. Pergamon Press, Oxford: 53–62.
- Flanagan, P. R., McLellan, J. S., Haist, J., Cherian, G., Chamberlain, M. J. & Valberg, L. S. 1978: Increased dietary cadmium absorption in mice and human subjects with iron deficiency. — *Gastroenterology* 74: 841–846.
- Fornstedt, B., Pileblad, E. & Carlson, A. 1990: In vivo auto-oxidation of dopamine in guinea pig striatum increases with age. — *J. Neurochem.* 55: 655–659.
- Förstner, U. & Wittmann, G. T. W. 1979: *Metal pollution in the aquatic environment*. — Springer-Verlag, Berlin.
- Francko, D. A. & Heath, R. T. 1982: UV-sensitive complex phosphorus: association with dissolved humic material and iron in a bog lake. — *Limnol. Oceanogr.* 27: 564–569.
- Furmańska, M. 1979: Studies of the effect of copper, zinc and iron on the biotic components of aquatic ecosystems. — *Pol. Arch. Hydrobiol.* 26: 213–220.
- Gerhardt, A. 1992: Effects of subacute doses of iron (Fe) on *Leptophlebia marginata* (Insecta: Ephemeroptera). — *Freshw. Biol.* 27: 79–84.
- 1995: Joint and single toxicity of cadmium (Cd) and iron (Fe) related to metal uptake in the mayfly *Leptophlebia marginata* (L.) (Insecta: Ephemeroptera). — *Hydrobiologia*. (In press).
- Gerhardt, A. & Westermann, F. 1995: Effects of precipitations of iron hydroxides on *Leptophlebia marginata* L. (Insecta: Ephemeroptera) in the field. — *Arch. Hydrobiol.* 133: 81–93.
- Gibson, R. & Barker, P. L. 1979: The decapod hepatopancreas. — *Oceanogr. Mar. Biol. Annu. Rev.* 17: 285–346.
- Giesy, J. P. Jr. 1976: Stimulation of growth in *Scenedesmus obliquus* (Chlorophyceae) by humic acids under iron limited conditions. — *J. Phycol.* 12: 172–179.
- Gore, J. 1985: *The restoration of rivers and streams. Theories and experience*. — Butterworth Publishers, London.
- Gower, A. M., Myers, G., Kent, M. & Foulkes, M. E. 1994: Relationships between macroinvertebrate communities and environmental variables in metal-contaminated streams in south-west England. — *Freshw. Biol.* 32: 199–221.
- Grieve, I. C. 1984: Relationships among dissolved organic matter, iron and discharge in a moorland stream. — *Earth Surf. Proc. Landf.* 9: 35–41.
- Hall, A., Valente, I. M. C. B. & Davies, B. R. 1977: The Zambezi River in Mozambique: The suspended solids régime and composition of the middle and lower Zambezi prior to the closure of the Cabora Bassa Dam. — *Freshwat. Biol.* 7: 187–206.
- Halliwel, B. & Gutteridge, J. M. C. 1984: Oxygen toxic-

- ity, oxygen radicals, transition metals and disease. — *Biochem. J.* 219: 1–14.
- Handy, R. D. 1993: The effect of acute exposure to dietary Cd and Cu on organ toxicant concentrations in rainbow trout, *Onchorhynchus mykiss*. — *Aquatic Toxicol.* 27: 1–14.
- Hare, L. 1992: Aquatic insects and trace metals: bioavailability, bioaccumulation and toxicity. — *Crit. Rev. Toxicol.* 22: 327–369.
- Hartikainen, H. & Yli-Halla, M. 1986: Oxidation-induced leaching of sulphate and cations from acid sulphate soils. — *Water Air Soil Pollut.* 27: 1–13.
- Heikkinen, K. 1990a: Transport of organic and inorganic matter in river, brook and peat mining water in the drainage basin of the river Kiiminkijoki. — *Aqua Fennica* 20: 143–155.
- Heikkinen, K. 1990b: Nature of dissolved organic matter in the drainage basin of a boreal humic river in Northern Finland. — *J. Environ. Qual.* 19: 649–657.
- Heikkinen, K. 1990c: Seasonal changes in iron transport and nature of dissolved organic matter in a humic river in Northern Finland. — *Earth Surf. Proc. Landf.* 15: 583–596.
- Heikurainen, L., Kenttämies, K. & Laine, I. 1978: The environmental effects of forest drainage. — *Suo* 29: 46–58.
- Hildén, M. & Rapport, D. 1994: Four centuries of cumulative cultural impact on a Finnish river and its estuary: An ecosystem health approach. — *J. Aquat. Ecos. Health*. (In press).
- Hynes, H. B. N. 1970: The ecology of running waters. — Univ. Toronto Press, Toronto.
- Johnson, C. A. & Thornton, I. 1987: Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage. — *Wat. Res.* 21: 359–365.
- Jones, K. G., Cole, F. M. & Sweeney, G. D. 1981: The role of iron in the toxicity of 2, 3, 7, 8-tetrachlorodibenzo(p) — dioxin (TCDD). — *Toxicol. Appl. Pharmacol.* 61: 74–88.
- Jonnalagadda, S. B. & Prasada Rao, P. V. V. 1993: Toxicity, bioavailability and metal speciation. — *Comp. Biochem. Physiol.* 106C: 585–595.
- Kawaguchi, H. & Inagaki, A. 1994: Kinetics of ferric ion promoted photocomposition of 2-chlorophenol. — *Chemosphere* 28: 57–62.
- Koenings, J. P. & Hooper, F. 1976: The influence of colloidal organic matter on iron-phosphorus cycling in an acid bog lake. — *Limnol. Oceanogr.* 21: 684–696.
- Letterman, R. D. & Mitsch, W. J. 1978: Impact of mine drainage on a mountain stream in Pennsylvania. — *Environ. Pollut.* 17: 53–73.
- Livingstone, D. A. 1963: Chemical composition of rivers and lakes. — In: *Fleischer, M. (Ed.), Data of Geochemistry*, 6 ed., U. S. Geol. Surv. Prof. Paper 440-G, 489 pp.
- Luckowicz, M. v. 1976: Der Eisengehalt in Wasser und seine Wirkung auf den Fisch. — *Fisch Umwelt* 2: 85–92.
- Luoma, S. N. 1983: Bioavailability of trace metals to aquatic organisms – A review. — *Sci. Total Environ.* 28: 1–22.
- Maltby, L. & Crane, M. 1994: Responses of *Gammarus pulex* (Amphipoda, Crustacea) to metalliferous effluents: identification of toxic components and the importance of interpopulation variation. — *Environ. Pollut.* 84: 45–52.
- Maltby, L., Snart, J. O. H. & Calow, P. 1987: Acute toxicity tests on the freshwater isopod, *Asellus aquaticus* using  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ , with special reference to techniques and the possibility of intraspecific variation. — *Environ. Pollut.* 43: 271–279.
- Martin, T. R. & Holdich, D. M. 1986: The acute lethal toxicity of heavy metals to peracarid crustaceans (with particular reference to fresh-water asellids and gammarids). — *Water Res.* 20: 1137–1147.
- McKnight, D. M. & Feder, G. L. 1984: The ecological effect of acid conditions and precipitation of hydrous metal oxides in a Rocky Mountain stream. — *Hydrobiologia* 119: 129–138.
- McKnight, D. M., Bencala, K. E., Zwellweger, G. W., Aiken, G. R., Feder, G. L. & Thorn, K. A. 1992: Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. — *Environ. Sci. Technol.* 26: 1388–1396.
- Obata, T., Hosokawa, H. & Yamanaka, Y. 1993: Effect of ferrous iron on the generation of hydroxyl free radicals by liver microdialysis perfusion of salicylate. — *Comp. Biochem. Physiol.* 106C: 629–634.
- Osmulski, P. A. & Leyko, W. 1986: Structure, function and physiological role of *Chironomus haemoglobin*. — *Comp. Biochem. Physiol.* 85B: 701
- Otto, C. & Svensson, B. S. 1983: Properties of acid brownwater streams in South Sweden. — *Arch. Hydrobiol.* 99: 15–36.
- Palko, J. 1994: Acid sulphate soils and their agricultural and environmental problems in Finland. — Dissertation, Acta Univ. Ouluensis, Series C, Technica 75, University of Oulu, Oulu, Finland. 58 + App.
- Parsons, J. D. 1968: The effects of acid strip-mine effluents on the ecology of a stream. — *Archs. Hydrobiol.* 65: 25–50.
- Patrick, F. M. & Loutit, M. W. 1978: Passage of metals to freshwater fish from their food. — *Water Res.* 12: 395–398.
- Peuranen, S., Vuorinen, P., Vuorinen, M. & Hollander, A. 1994: The effects of iron, humic acids and low pH on the gills and physiology of Brown Trout (*Salmo trutta*). — *Ann. Zool. Fennici* 31: 389–396.
- Rasmussen, K. & Lindegaard, C. 1988: Effects of Fe compounds on macroinvertebrate communities in a Danish Lowland River Stream. — *Water Res.* 22: 1101–1109.
- Scullion, J. & Edwards, R. W. 1980: The effects of coal industry pollutants on the macro-invertebrate fauna of a small river in the South Wales coalfield. — *Freshw. Biol.* 10: 141–162.
- Sheldon, S. P. & Kelly, D. K. 1990: Differential coloniza-

- tion and growth of algae and ferromanganese-depositing bacteria in a mountain stream. — *J. Freshw. Ecol.* 5: 475–485.
- Simkiss, K. & Taylor, M. G. 1989: Metal fluxes across the membranes of aquatic organisms. — *Crit. Rev. Aquat. Sci.* 1, 173.
- Smith, E. J., Sykora, J. L. & Shapiro, M. A. 1973: Effect of lime-neutralized iron-hydroxide suspensions on survival, growth and reproduction of the fathead minnow (*Pimephales promelas*). — *J. Fish. Res. Board Canada* 30: 1147–1153.
- Smith, E. J. & Sykora, J. L. 1976: Early developmental effects of lime-neutralized iron-hydroxide suspensions on brook trout and coho salmon. — *Trans. Amer. Fish. Soc.* 105: 308–312.
- Snowden, R. E. D. & Wheeler, B. D. 1993: Iron toxicity to fen plant species. — *J. Ecology* 81: 35–46.
- Stevens, R. G. & Kalkwarf, D. R. 1990: Iron, radiation and cancer. — *Environ. Health Persp.* 87: 291–300.
- Steffens, W., Mattheis, T. & Riedel, M. 1992: Field observations on the sensitivity of rainbow trout (*Oncorhynchus mykiss*) to high concentrations of water-borne iron. — *EIFAC/XVII/92/Symp.* E39. 11 pp.
- Sulzberger, B., Schnoor, J. L., Giovanoli, R., Hering, J. G. & Zobrist, J. 1990: Biogeochemistry of iron in an acidic lake. — *Aquatic Sciences* 52: 56–74.
- Theis, T. L. & Singer, P. C. 1974: The stabilization of ferrous iron by organic compounds in natural waters. — In: Singer, P. C. (ed.), *Trace metals and metal-organic interactions in natural waters*: 303–320.
- Thorup, J. 1966: Substrate type and its value as a basis for the delimitation of bottom fauna communities in running waters. *Spec. Publ., Pymatuning Lab. Fld. Biol.* 4: 59–74.
- Tipping, E. 1981: The adsorption of aquatic humic substances by iron oxides. — *Geochim. Cosmochim. Acta* 45: 191–199.
- Updegraff, K. F. & Sykora, J. L. 1976: Avoidance of lime-neutralized iron hydroxide solutions by coho salmon in the laboratory. — *Environ. Sci. Technol.* 10: 51–54.
- Vogt, G. & Qunitio, E. T. 1994: Accumulation and excretion of metal granules in the prawn, *Penaeus monodon*, exposed to water-borne copper, lead, iron and calcium. — *Aquatic Toxicol.* 28: 223–241.
- Vuori, K.-M. 1993: Influence of water quality and feeding habits on the whole-body metal concentrations in lotic trichopteran larvae. — *Limnologica* 23: 301–308.
- 1995: Species and population specific responses of translocated hydropsychid larvae (Trichoptera, Hydropsychidae) to runoff from acid sulphate soils in the river Kyrönjoki, Western Finland. — *Freshw. Biol.* 33: 305–318.
- Walter, G. 1966: Ökologische Untersuchungen über die Wirkung Fe-II haltiger Braunkohlegruben-Abwässer auf Vorfluterorganismen. — *Wissensch. Zeit. Karl-Marx-Universität, Leipzig* 15, 1: 247–269.
- Warnick, S. & Bell, H. L. 1969: The acute toxicity of some heavy metals to different species of aquatic insects. — *J. Water Pollut. Contr. Feder.* 41: 280–284.
- Wartiovaara, J. 1978: Phosphorus and organic matter discharged by Finnish rivers to the Baltic Sea. — *Publ. Water Res. Instit., Nat. Board Waters, Finland*: 29.
- Weatherley, N. S., Rutt, G. P., Thomas, S. P. & Ormerod, S. J. 1991: Liming acid streams: aluminium toxicity to fish in mixing zones. — *Water Air Soil Pollut.* 55: 345–353.
- Wellnitz, T. A., Grief, K. A. & Sheldon, S. P. 1994: Response of macroinvertebrates to blooms of iron-depositing bacteria. — *Hydrobiologia* 281: 1–17.