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# Iron and manganese cycling in the storm runoff of a Scottish upland catchment

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**Abstract**

Factor analysis and (two-component) end member mixing analysis (EMMA) were applied to high resolution stream chemistry data from three catchments to infer sources of iron and manganese-rich runoff in the catchment area and to evaluate their temporal and spatial influence on the stream water quality. The results demonstrate that flow related changes in soilwater inputs (associated with changes in flow pathways) exert a major control on stream chemistry during storm events and depend on the soil distribution in the catchments as well as on antecedent conditions and storm intensity. Two Fe and Mn sources were identified: (1) an organic soilwater source, associated with Fe and Mn accumulation in the organic-rich upper soil horizons; and (2) a deep soilwater/groundwater source arising from reduced metal mobilisation in the deeper soils. While (1) provides the dominant inputs during storm events, (2) becomes important just before peak flow when riparian groundwater is displaced into the stream giving rise to total Fe and Mn concentrations of up to 1160 and 121 $\mu g\ l^{-1}$, respectively. The timing of such high Fe and Mn loadings in the stream runoff has important implications for the water supply management of the catchment. Subsequent effects on lakes/reservoirs, for example, must be considered when assigning load limits or load reduction goals for the purpose of improving/ maintaining water quality but also when planning maintenance work on the reservoir. However, a better understanding of the nature of these Fe and Mn sources is required to better (quantitatively) predict when and where undesirable Fe and Mn concentrations will occur.


*Keywords:* Hydrology; Iron; Manganese; Factor analysis; EMMA; Scotland

## 1. Introduction

Upland areas constitute an important component of the natural heritage of Scotland and provide the headwaters of many major river systems. As such, upland catchments are the major sources of potable, industrial and agricultural water supplies, particularly in Scotland where 96% (by volume) of the public water supplies are derived from surface waters (MacDonald, 1994).

While generally regarded as relatively undisturbed natural environments, increasing environmental pressures on upland water quality arise from

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acidification through sulphur and nitrogen deposition (Kirchner and Lydersen, 1995; Neal et al., 1998), high sediment loads from forestry and overgrazing (Carling et al., 2001) and mobilisation of colour and metals (Mitchell and McDonald, 1995). This has provided a major impetus for water quality research in the UK during the last few decades. Much research has been undertaken in upland catchments in Wales (Neal et al., 1997a) and North-East Scotland (Soulsby et al., 1998; 2003) and the results have significantly improved the understanding of the water quality functioning in such upland environments (Langan et al., 2001; Neal et al., 2004).

While iron (Fe) and manganese (Mn) have been included in many of these studies on upland catchment hydrogeochemistry (Reid et al., 1981; Giusti and Neal, 1993; Heal, 2001), the main research focus has been on the impact of acid deposition and aluminium mobilisation. Comparatively little work has been dedicated to water quality problems related to the occurrence of background high loadings of Fe and Mn, probably because of their, generally, less harmful effect compared to inorganic aluminium species. However, at high concentrations, Mn toxicity to fish (Nyberg et al., 1995) and humans (Kondakis et al., 1989) has been suggested, and high Fe levels can also have ecological impacts, such as destruction of fish spawning grounds (Marsden and Mackay, 2001) and smothering of benthos with iron hydroxides (Younger, 2001). Moreover, the increased presence of Fe and Mn in stream runoff and water bodies is of growing concern to many water authorities in the UK (Little and McFadzean, 1991; Schofield et al., 1991; Graham et al., 2002) and the EC Drinking Water Directive (CEC, 1980) has set the mandatory maximum admissible concentration of Mn and Fe in drinking water at 50 and 200 $\mu g\, l^{-1}$, respectively. Although only about one per cent of the drinking water samples tested across Scotland in 1996 failed to meet these EC Standards for Mn, the majority of failures occurred in upland terrains (Heal, 2001). Temporary deterioration in Mn quality, for example, has occurred in the raw waters of Loch Bradan, south-west Scotland (Little and McFadzean, 1991), and Fe and Mn problems were also experienced in the Megget Reservoir during an excessive draw down of the water level in 1997/98 (Abesser, 2003).

Elevated Mn and Fe concentrations in streams and water bodies are commonly observed in upland regions and have been reported in a number of studies in Scotland (Reid et al., 1981; Giusti and Neal, 1993; Gavin et al., 2001), northern England (Stunell and Younger, 1995) and Wales (Neal et al., 1997a). The high Mn and Fe concentrations are generally associated with the acidic pH and the organic nature of the poorly drained peaty upland soils, which favour mobilisation of Mn and Fe. However, relatively little is known about the mechanisms and pathways by which these elements are delivered to streams.

Catchment hydrology is a dominant control on stream water quality and metal loading, and long-term monitoring of individual streams and catchments has been invaluable in understanding the complexity of the underlying hydrological processes. However, the majority of these studies have relied on weekly to monthly sampling regimes and spot sampling at such large intervals tends to overlook peak values and details of changes in stream chemistry during events (Peters, 1994; Jarvie et al., 2001), which are often rapid, due to the 'flashy' runoff response characteristic of most upland catchments. Large changes in flow and associated chemistry can occur in a matter of hours or minutes (Foster et al., 1997) and are often associated with high loadings in colour (TOC), Fe and Mn (Reid et al., 1981; Giusti and Neal, 1993; Neal et al., 1997a; Heal et al., 2002). Hence, sample collection at time scales that more closely correspond to the hydrological dynamics of the system is essential in documenting the main chemical effects associated with the rapid stream response to events and is also important for capturing the entire range of stream chemical loadings (Kirchner et al., 2004). Short-term intensive sampling during storms thereby provides insight into the hydrochemical response of individual streams/catchments to changing hydrological conditions and this allows identification of critical periods of acidic runoff and/or high metal (e.g. Fe, Mn) loading. This knowledge is essential for effective water quality management in upland catchments (Heal et al., 2002) and also for the development of future protection, management and operation strategies for increasingly vulnerable upland water supply bodies.