Increasing concentrations of arsenic and vanadium in (southern) Swedish streams

Teresia Wällstedt^{a*}, Louise Björkvald^a, Jon Petter Gustafsson^b

^aDepartment of Aquatic Sciences and Assessment, SLU (Swedish University of Agricultural Sciences) , P.O. Box 7050, SE-750 07 Uppsala, Sweden

^bDepartment of Land and Water Resources Engineering, KTH (Royal Institute of Technology), Teknikringen 76, SE-100 44 Stockholm, Sweden

*Corresponding author, present address: Department of Geological Sciences, Stockholm University, SE-106 91 Stockholm. E-mail address: teresia.wallstedt@geo.su.se (T. Wällstedt) Phone.: +46-8-674 78 35.

Abstract

The aim of this study was to investigate temporal trends and controlling factors of As and V in running waters throughout Sweden. For this purpose, data on stream water chemistry from 62 streams of varying catchment size and characteristics, included in the Swedish environmental monitoring programmes were evaluated. The geochemical software Visual MINTEQ was used to model the speciation and trend analyses were performed on total concentrations of As and V as well as modelled fractions (dissolved species as well as arsenate and vanadate adsorbed to ferrihydrite). The trend analyses showed increasing total concentrations of As and V in southern Sweden. Concentrations of As and V correlated significantly to Fe concentrations in 59 and 60 of the 62 streams respectively, indicating that Fe is an important determining factor for As and V concentrations in Swedish streams. This was confirmed by the geochemical modelling that indicated that the adsorbed fraction is the dominant form of As and V and that the concentrations of As and V in Swedish streams are thus highly determined by concentrations of colloidal or particulate Fe. It is therefore suggested that the increasing trends of As and V are to a large extent due to increasing concentrations of colloidal Fe, which is stabilised by increasing concentrations of DOC. Further the geochemical modelling indicates that the dissolved fraction of As and V generally is small, with the exception of a few streams with high pH and/or phosphate concentrations.

1. Introduction

Arsenic is widely recognised as a hazardous contaminant and as a threat to some of the world's water resources (Smedley and Kinniburgh, 2002) and numerous studies have focused on problems with high As concentrations in groundwater in e.g. Bangladesh (Anawar et al.,

2003). Because of the potential toxicity to biota, even low concentrations of some trace metals and metalloids, such as As, are of interest in surface waters. Due to the chemical similarity of arsenate to phosphate, As may be especially harmful to phytoplankton in phosphate-limited, oligotrophic ecosystems, where concentrations as low as 2 µg/L may cause negative effects (Blanck et al., 1989; Lithner, 1989). Vanadium has received much less attention, but shows chemical similarities to As and has also been reported as being toxic to biota (Perez-Benito, 2006; Sternbeck and Östlund, 1999).

Arsenic is often present as a minor component in common rock-forming minerals and relatively large concentrations may for example occur in sulphide minerals, e.g. pyrite. High As concentrations can also be found in oxide minerals and hydrous metal oxides, especially when they have formed as oxidation products of primary Fe sulphide minerals. Arsenic is also a known contaminant, released by smelter operations and fossil-fuel combustion (Smedley and Kinniburgh, 2002). Redox potential (pe) and pH are the most important factors controlling the speciation of As. Arsenic(V), arsenate, is the predominant form in well oxidised waters while As(III), arsenite, dominates in reduced environments (Raven et al., 1998; Smedley and Kinniburgh, 2002).

Vanadium is widely distributed in the earth's crust and is frequently found in P ores (Jansson-Charrier et al., 1996). Vanadium is also the major trace metal in petroleum products and is thus emitted to the atmosphere when fossil fuels are burned (Jacks, 1976). Vanadium occurs as V(III), V(IV) and V(V) in aqueous solution, where V(V), vanadate, is stable in oxic water (Naeem et al., 2007).

The chemical speciation is important for the toxicity of metal(oid)s. Metal ions can be complexed to humic substances, or adsorbed to oxides (e.g. Fe, Mn and Al oxides) and may thus be bound to colloids and/or particles that contain these constituents (Lofts and Tipping, 2000). This makes the metal ions less available for direct uptake and therefore less toxic to aquatic biota. At neutral pH and oxic conditions, arsenic is effectively immobilized by sorption or co-precipitated with metal oxides, mainly Fe oxides, but also oxides of e.g. Mn and Al (Gupta and Chen, 1978; Rothwell et al., 2009; Smedley and Kinniburgh, 2002). Vanadate, like arsenate, is strongly adsorbed to Fe oxides (Blackmore et al., 1996; Naeem et al., 2007) and possibly also other metal oxides. This implies that changes in the concentrations of particulate or colloidal Fe may influence the concentrations of As and V in surface waters.

Increasing concentrations of Fe, correlated to increasing concentrations of dissolved organic matter (DOM) have been reported from the UK (Neal et al., 2008). The authors propose that the increase is due to increasing concentrations of micro-particulate Fe(III) which is stabilised against aggregation by binding of DOM to the particle surface. Trends of Fe in running waters in Sweden have not been thoroughly studied, but general increasing trends for dissolved organic C (DOC) concentrations have been reported from many areas in

Europe, including Sweden, and North America (e.g. Evans et al., 2005; Skjelkvåle et al., 2005). The mechanisms for this increase is not fully understood, but a combination of declining acid deposition, rising temperatures and increased surface runoff has been suggested (e.g. Erlandsson et al., 2008; Evans, 2005; Evans et al., 2005; Freeman and Fenner, 2001; Monteith et al., 2007; Tranvik and Jansson, 2002)

Increasing DOC concentrations may influence the mobility of As and V in the environment, since fulvic or humic acids form stable complexes with mineral surfaces, hence inhibiting As from adsorption onto for example Fe oxides (Grafe et al., 2002). Further, recovery from acidification with increasing pH in stream water may enhance the mobility of As and V since they are more mobile at neutral or high pH. On the other hand, deposition rates of elements such as As and V have decreased throughout Europe during the last decades due to reduced anthropogenic emissions (Harmens et al., 2007; Rühling and Tyler, 2001). Several different processes may thus influence the mobility and concentrations of As and V in the Swedish environment.

To assess potential impacts of As and V, of both anthropogenic and natural origin, on sensitive ecosystems it is crucial to investigate trends and to understand the controlling factors for these elements in stream water. In this context, time series concentrations of As and V available from the Swedish environmental monitoring programmes, including streams of varying catchment size and characteristics, provide a unique source of data which allows for investigation of temporal trends on a large geographical scale.

The aim of this study was to investigate temporal trends and the controlling factors for As and V in running waters throughout Sweden. In order to better understand the regulation of As and V concentrations in the streams, the geochemical model Visual MINTEQ was used in an attempt to determine the speciation of As and V. Several studies have shown that geochemical models like MINTEQ, WHAM and PHREEQC generally predict the dominant metal species with reasonable accuracy (e.g. Davis et al., 1994; Lumsdon et al., 2001; Sracek et al., 2004; Unsworth et al., 2006). In the present study, we used a modelling approach similar to the one used recently by Sjöstedt et al. (2009), who found reasonable agreement between dialysis results for 3 lakes and a model that considered trace metal binding to DOM as well as to colloidal ferrihydrite.

2. Materials and methods

2.1. Study area and sampling

Existing data from streams in the Swedish national monitoring programmes were used for this study. A number of criteria had to be fulfilled in order for the stream to be included; in addition to continuous data on concentrations of As and V, concentrations of Fe, Mn and total organic C (TOC) were also required. As a result, 62 streams were chosen with continuous water chemistry data encompassing the period 1998-2007 (44 streams) or 2001-2007 (18

streams). The dataset includes most of Sweden's large rivers (Table 1, Fig. 1) as well as some small ones, and together they drain the major part of Sweden. The sampling points are in many cases close to the river mouths, thus integrating influences from the entire watershed.

The streams are considered to be relatively unaffected by local point sources and are situated throughout Sweden. They are very variable in terms of e.g. size of drainage area (ranging from 1-50 000 km²), mean pH (4.4-7.9) and mean TOC concentration (1.5-20 mg l⁻¹) (Table 1). All streams have been sampled at least monthly and the data is freely available from the data host (Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment) at <http://www.ma.slu.se/>.

2.2. Chemical analyses

All water chemical analyses were performed using national or international standard methods, when applicable and all analyses followed quality control routines, defined in the accreditation of the laboratory at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences. The samples were sent by mail to the laboratory, immediately after sampling and generally arrived on the following day. Alkalinity and pH were generally analysed within 24 h of sampling. The pH was determined according to the Swedish standard method SS 02 81 22-2 (modified), the pH electrode was calibrated with pH 4 and 6 buffer solutions. The alkalinity was determined following the international standard method SS-EN-ISO 9963-2, by titration with HCl to pH 5.4, with continuous removal of the CO₂ formed, using N₂ gas. Major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) were determined using ICP while major anions (SO₄²⁻, Cl⁻, F⁻) were determined by ion chromatography. Phosphate was determined using a *Bran+Luebbe Autoanalyzer 3*. Total organic C was determined on unacidified samples by oxidative combustion with a *Shimadzu TOC 5050 Analyzer*. Samples for determinations of monomeric Si were preserved with H₂SO₄ and analysed on a *Technicon Traacs 800*. Metal concentrations were determined by ICP-MS on samples that were preserved with 0.5% ultrapure HNO₃ on arrival at the laboratory. Determined metal concentrations represent total concentrations, since the samples were not filtered in the field or in the laboratory.

2.3. Modelling

The geochemical software code Visual MINTEQ (Gustafsson, 2007, <http://www.lwr.kth.se/English/OurSoftware/vminteq/>) was used to model the metal speciation. For inorganic complexes, the thermodynamic default database in Visual MINTEQ was used, which is mostly based on the NIST compilation (Smith et al., 2003).

Complexation with dissolved organic matter (DOM) was modelled using the SHM (Stockholm Humic Model) (Gustafsson, 2001), assuming that 100 % of the DOM consisted of fulvic acid. The values for TOC were assumed to be the same as dissolved (<0.45 µm)

organic C (DOC), since they differ by less than 5% for stream water in Fenno-Scandian boreal forest areas (Temnerud et al., 2007). The SHM was needed to calculate the partitioning of Fe between colloidal ferrihydrite and the dissolved phase, as dissolved Fe(III)-organic complexes represent important Fe species in natural waters. In the SHM complexation constants for monomeric Fe(III)-organic complexes according to van Schaik et al. (2010) were used. Furthermore the model also considers the complexation of V(IV) to DOM, using results obtained for V(IV) binding to soil organic matter (Gustafsson et al., 2007).

The input to Visual MINTEQ included concentrations of major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (SO_4^{2-} , Cl^- , F^- , PO_4^{3-} and alkalinity), pH, Si, TOC and the elements Fe, Mn, Cu, Zn, Al, Pb, Cr, As and V. The temperature was set constant to 10°C.

The redox potential (pe) is important for the speciation of Fe, As and V and is thus important to consider in the modelling. No determination of pe was available, but in O_2 -saturated waters a reasonable pe value can be estimated with the following formula (Stumm and Morgan, 1996):

$$\text{pe} = 20.78 + 1/4 \log P_{\text{O}_2} - \text{pH} \quad (1)$$

An O_2 pressure of 0.2 atm was assumed.

In the modelling, the redox potential for each stream was set to the average pe for all samples in that stream. Average pe-values were between 12.7 (Råån) and 16.2 (Lommabäcken). These values should be considered as maximum values, since the redox reaction for O_2 is slow and the pe-values of natural waters are in reality often lower than the theoretical values (Langmuir, 1997).

As a first step, redox modelling was made with the aim of investigating the influence of varying pe on the speciation of Fe, As and V. Average values of the input parameters from selected streams with different pH (4.45 – 7.9) were entered and pe was varied between 5-17 in the MINTEQ runs. The redox couples Fe(III)/Fe(II), As(III)/As(V) (as $\text{H}_3\text{AsO}_3/\text{AsO}_4^{3-}$) and V(IV)/V(V) (as $\text{VO}^{2+}/\text{HVO}_4^{2-}$) were allowed in the model.

For modelling of adsorption, ferrihydrite, $\text{Fe}_2\text{O}_3 \cdot 1.8\text{H}_2\text{O}$, was specified as the possible solid phase, meaning that Visual MINTEQ allowed precipitation of this solid. The solubility constant selected was one for ‘aged’ ferrihydrite with $\log *K_s = 2.69$ at 25°C (Smith et al., 2003). This is in the lower range of constants reported for “amorphous iron hydroxide”, “hydrous ferric oxide”, etc. ($\log *K_s = 2.5$ to 5; Tipping et al., 2002).

Adsorption to ferrihydrite was estimated using the Diffuse layer model (Dzombak and Morel, 1990) (available in the Visual MINTEQ software as “HFO with DLM”). The database used includes constants for arsenate calculated from several different data sets (Gustafsson and Bhattacharya, 2007).

Adsorption constants for vanadate to ferrihydrite were not available in the database. Therefore adsorption constants were estimated using a dataset published by Blackmore et al., (1996), including competitive adsorption of vanadate and phosphate on Fe oxyhydroxide. The constants found were:

The fit of the modelling results to that of the laboratory results of Blackmore et al. (1996) are shown in Figures S1-S3 in the online supplementary information and the adsorption constants used for arsenate, vanadate and phosphate are shown in Table S1 in the online supplementary information.

In this study it was not possible to consider adsorption of V(IV) to ferrihydrite, since no data set could be found in the literature that quantitatively described this interaction.

2.4. Statistical methods

For trend analyses, Seasonal Kendall with Covariance Inversion for correction of serial correlation, described by Loftis et al. (1991) was used to test the significance of trends. This non-parametric method was used since the data were autocorrelated in time with a strong seasonal variation. Further, the method can be used on data that are not normally distributed, which is commonly the case with environmental data and it is also robust for extreme values and possible outliers (Helsel and Hirsch, 1992). The Seasonal Kendall has also been shown to be reliable in comparison with other methods for trend analysis and to maintain a high power with different trend functions (Hess et al., 2001).

Since the streams have been sampled monthly, each month was treated as a separate season. When several samples from one season were present, the first value from that season was automatically chosen. Mean or median values were not used because that would influence the variance in the dataset (Helsel and Hirsch, 1992). For the magnitude of the trend, Theil's slope (Helsel and Hirsch, 1992) was estimated for the time series of each season and the slope was then estimated as the average of the seasonal Theil's slopes. Since the Theil's slopes are calculated on a yearly basis, the result will show the increase or decrease per year, i.e. for a element that has the concentration unit $\mu\text{g L}^{-1}$, the Theil's slope will have the unit $\mu\text{g L}^{-1} \text{ a}^{-1}$.

A two-tailed sign test was then used to investigate possible underlying trends in the whole stream population. If there is no underlying trend, the Theil's slope estimates for a certain variable (regardless of significance level for the trend in each separate stream) would be expected to display a binomial distribution with about 50% negative and 50% positive slopes.

This was used to calculate the statistical probability that a certain number of streams show slopes in one direction (positive or negative) while the resulting streams have estimated slopes in the other direction. For example, for Fe only 2 out of 32 streams in southern Sweden show negative Theil's slope estimates. The two tailed sign test is then used to calculate the probability that only 0, 1 or 2 streams have estimated slopes in one direction (positive or negative) while the rest of the streams have slopes in the other direction when the null hypothesis is that there is no general trend affecting the slope estimates.

3. Results

3.1. Relationships between dissolved As/V and water chemistry

The influence of pH, Fe and TOC on the observed concentrations of As and V were evaluated by linear regressions using pH and concentrations of Fe and TOC as controlling variables. All concentration data were log-transformed to better approach normal distribution.

The correlation between As and Fe was positive and significant ($p < 0.05$) in 59 of the 62 streams (exemplified in Fig. 2). In 27 of these streams the correlation was strong ($r^2 > 0.5$). The correlation between As and TOC was also positive and significant ($p < 0.05$) in 53 of the 62 streams and the correlation was strong ($r^2 > 0.5$) in 10 of the streams. Linear regressions between As and pH showed weak but significant correlations in 37 streams. These correlations were however both positive and negative and no correlations had $r^2 > 0.5$.

Vanadium showed a positive correlation with Fe (exemplified in Fig. 2) and the correlation was significant in 60 of the 62 streams ($p < 0.05$). In 34 of the streams there was a strong correlation ($r^2 > 0.5$), and in 6 of these streams the correlation was very strong ($r^2 > 0.9$). There was also a positive correlation between V and TOC and the correlation was significant ($p < 0.05$) in 53 streams with $r^2 > 0.5$ in 6 of the streams. Significant correlation between V and pH was observed in 41 of the streams. These were generally negative, but positive correlations were sometimes also observed. Of these only one correlation was strong ($r^2 > 0.5$).

Further, Fe showed a significant ($p < 0.05$) positive correlation with TOC in 53 of the streams and this correlation was strong ($r^2 > 0.5$) in 10 streams.

3.2. Modelling results

Iron is sensitive to changes in pe, which means that the amount of ferrihydrite, i.e. the carrier surface for adsorbed arsenate and vanadate may decrease at low pe values. However, the initial redox modelling indicated no significant decrease in the amount of precipitated ferrihydrite at $pe > 5$ when pH was around 6 or higher, $pe > 8$ at $pH > 5$ and $pe > 10$ at $pH > 4.5$. These pe values are relatively far from the estimated pe values (for information on pe estimation, see the modelling section in the material and methods section) and we are

therefore confident that the uncertainties in the pe estimates do not have any significant impact on the modelling results for ferrihydrite.

For vanadium, V(V) dominated completely over V(IV) according to the model. However, the initial calculations with varying pe indicated that V(IV) may be present in significant amounts (more than a few percent of the total V concentration) at $pe < 13.5$ when pH is around 4.5, $pe < 10.5$ at pH = 5 and $pe < 5.5$ at pH 6. These pe values are lower than the estimated pe-values at each pH, but since the pe estimates should be considered as maximum values, as mentioned in the methods section, V may to a small extent be present as V(IV) in the acidic ($pH \leq 5$) streams. When V(IV) is present, it is modelled as entirely bound to DOM.

For the redox couple H_3AsO_3/AsO_4^{3-} , the redox modelling suggests that As(V) is totally dominant and that As(III) is not likely to be present in significant amounts in the pH interval of the studied streams.

At pH-values above 5.5, Fe was almost entirely modelled as particulate/colloidal, i.e. precipitated as ferrihydrite, with < 2 -3% of the total Fe concentration dissolved. At pH-values below 5.5, a higher percentage of the total Fe concentration was modelled as dissolved, up to around 20% on average (Table 2) or 35% at some occasions in the most acidic streams.

The fractions of As and V adsorbed to Fe were totally dominant (average ≥ 95 %) over the dissolved fraction in 2/3 (41 out of 62) of the streams according to the modelling results (Table 2). These were acidic or neutral pH streams, with mean pH of 4.4-7.1 and included streams with small and large drainage areas (1-40 000 km²) showing both increasing trends and insignificant or decreasing trends.

The remaining 21 streams had significant fractions (average > 5 %, Table 2) of dissolved As or both As and V according to the modelled speciation. These were all streams with mean pH above 6.9. In two of the streams, Råån and Kävlingeån, with mean pH of 7.9 and 7.8, respectively, and high concentrations of PO_4^{3-} (Tables 1 and 2), the dissolved free fraction of As was generally dominant over the adsorbed fraction while the dissolved free fraction was dominant occasionally in several streams.

The calculated charge differences were within the expected range, generally below 5% but larger differences (up to 12%) occurred for some samples.

3.3. Trend analyses

In general, pH showed slightly increasing trends across Sweden during the studied periods (Fig. 3). Even though the increasing trends were significant in only 7 of the 62 streams, the fact that 50 of the 57 streams with detectable slopes show increasing concentrations indicates a general positive trend over the whole stream population and this is also confirmed with the two-tailed sign test. The probability for a distribution with only 7 or fewer out of 57 slopes pointing in one direction is $< 10^{-8}$, i.e. the general pattern is highly

significant. The general trend is also significant if southern and northern Sweden are tested separately ($p < 10^{-3}$ and 10^{-5} respectively).

A similar picture emerges for Fe, where the significant trends all have positive slopes and only 15 streams of 59 with detectable slopes in the whole stream population have negative Theil's slope estimates. This result indicates a general increase in stream water Fe concentrations (two-tailed sign test, $p < 10^{-3}$). For southern Sweden, only 2 out of 32 streams have negative slope estimates which indicates a highly significant pattern (two-tailed sign test, $p < 10^{-6}$) while there is no significant general trend in northern Sweden (two-tailed sign test, $p = 1.0$).

For TOC, the general trend is not significant when the entire stream population is investigated, but for the 28 southern streams with detectable slopes, only 5 show negative slopes (two-tailed sign test, $p < 10^{-3}$). pH thus shows a general increasing pattern over the entire stream population, while Fe and TOC show significant increasing trends in the southern stream population (Fig. 3).

Total As concentrations are generally increasing, especially in southern Sweden (Figs 4 and 5a), with concentration increases of up to $27 \text{ ng L}^{-1} \text{ a}^{-1}$. In 21 of the 32 streams located in southern Sweden, increasing Theil's slope estimates of total As concentrations were observed. In 11 of these 21 streams the trend was significant ($p < 0.05$). The two-tailed sign test indicates that the general increasing trend for As is significant in the southern part of the country ($p < 10^{-6}$), while there is no significant general trend in the northern stream population ($p = 1.0$).

Total concentrations of V are generally increasing, with the most pronounced increase (up to $68 \text{ ng L}^{-1} \text{ a}^{-1}$) and the highest significance in southern Sweden (Fig. 6a). In 29 of the 32 streams in southern Sweden the Theil's slope estimates are positive and the increase is significant in 10 of these 29 streams. The two-tailed sign test indicates significant trends in V concentrations for the whole stream population as well as for southern and northern Sweden separately ($p < 10^{-9}$, 10^{-7} and 10^{-2} , respectively), but with the most pronounced increase in the southern part of the country.

The trend analyses of the fractions of As and V modelled as adsorbed to ferrihydrite show that there is an increase in the adsorbed fraction for As as well as for V (Figs 5b and 6b). Similarly to the total concentrations, this general increasing pattern is significant in southern Sweden for both As and V (two-tailed sign test, $p < 0.05$ and $p < 10^{-5}$, respectively), while significant increase in the dissolved fraction of As and V is found only in a few streams (Figs 5c and 6c).

4. Discussion

4.1. Relationships between dissolved As/V and water chemistry

The significant positive correlation observed between Fe and both As and V (59 and 60 of 62 streams) indicates that the transport of these elements in stream water to a large extent is

due to interactions with Fe (colloids). This interaction is most likely stronger for V than for As, which is indicated by the higher correlation of V to Fe. The positive correlation between As and Fe was expected, since it is well established that the presence of Fe particles and colloids strongly determines As concentrations at neutral pH and oxic conditions (Gupta and Chen, 1978; Rothwell et al., 2009; Smedley and Kinniburgh, 2002). Laboratory experiments have shown that vanadate also adsorbs strongly to Fe oxides (Blackmore et al., 1996; Naeem et al., 2007) and V has also been found to be associated with an Fe carrier phase in natural water (Dahlqvist et al., 2007).

Both As and V also showed positive correlation with TOC in 53 of the 62 streams. This indicates that organic matter may also be an important influencing factor for As and V transport and concentrations in Swedish streams. However, Fe also shows a positive correlation with TOC in 53 streams. In 5 of the 9 streams where Fe and TOC do not correlate, there is also no significant correlation between TOC and either As, V or both. Further, 6 of the 10 streams with strong correlation between Fe and TOC also show strong correlations between TOC and either As, V or both. This indicates that the correlation between As and V with TOC may not be causal, but instead a result of the correlation of As and V with Fe and the correlation of Fe with TOC. To be able to separate these processes from each other and unravel the causal factors, the concentrations of different As and V species would need to be known. Since no speciation measurements are available for the Swedish environmental monitoring data, it was necessary to use the best available knowledge, i.e. a geochemical model, to estimate the species concentrations.

4.2. Modelled speciation

At pH-values above 5.5, Fe was modelled as almost entirely precipitated, with a maximum dissolved fraction of 2-3% of the total Fe concentration (Table 2). This is in accordance with the results of Neal et al. (2008), who used WHAM/model VI to model the speciation of Fe in UK upland waters. They estimated the particulate fraction in one stream to 93% at baseflow and pH 6.5. In the present study, at pH-values below 5.5, a higher percentage of the total Fe concentration was modelled as dissolved, up to around 30% in the most acidic streams, due to the higher mobility of Fe at low pH.

For both As and V, a large proportion (> 95 %) of the total concentration is modelled as adsorbed to ferrihydrite in streams with mean pH below 7 (Table 2). A slight decrease in the adsorbed fraction can be noticed at very low pH-values (<4.8), probably as a result of the increased mobility of Fe at low pH-values and thus a smaller particulate Fe fraction in the most acidic streams (Bauer and Blodau, 2006). At higher pH (> 7) the adsorbed fraction decreases, especially at pH-values above 7.2-7.3 (Tables 1 and 2) and in the streams with highest mean pH (Råån and Kävlingeån), the adsorbed fraction is small (Table 2). This is probably, at least partly, due to the fact that adsorption of anions, like arsenate and vanadate,

decreases at increasing pH (Dzombak and Morel, 1990). This behaviour is also evident from adsorption experiments for both As (e.g. Raven et al., 1998) and V (Blackmore et al., 1996).

It is well known that As is associated with Fe and adsorption to other metal oxides, e.g. Al and Mn oxides has also been reported (Gupta and Chen, 1978; Rothwell et al., 2009; Smedley and Kinniburgh, 2002; Sracek et al., 2004). This association with Fe is also indicated in the present study since there is a significant correlation between As and Fe in many of the streams. The correlation with Fe is even stronger for V. In a study of colloidal trace elements in the Kalix river, also included in the present study (as Kalix älv), it was suggested that V was present in the river as vanadate and was strongly associated with a Fe carrier phase (Dahlqvist et al., 2007), while the association to C colloids was very weak. This is in agreement with the modelling results in the present study (Table 2).

When discussing the adsorption of arsenate and vanadate to Fe in the present study, it should be kept in mind that ferrihydrite was used as a proxy for several possible Fe oxides. This is of course a simplification, in reality the particulate/colloidal Fe fraction is probably a mixture of different oxides/hydroxides, of which all do not necessarily behave exactly like ferrihydrite.

As was mentioned earlier, an uncertainty in the results is that the adsorption of V(IV) to ferrihydrite could not be considered. However, given that V(IV), although strongly complexed to DOM, was predicted to be quite unstable relative to V(V) in the studied waters it seems unlikely that consideration of ferrihydrite-bound V(IV) would alter the main trends of the V results.

It is a well established fact that in the presence of anions like PO_4^{3-} , SO_4^{2-} and HCO_3^- , As sorption is reduced by competition for sorption sites (Appelo et al., 2002; Manning and Goldberg, 1996; Smith et al., 2002). Competition with PO_4^{3-} is probably a contributing factor for the relatively low adsorbed fractions of As in Tidån, Dalbergsån, Lidån, Nossan, Råån and Kävlingeån, which have high PO_4^{3-} concentrations, combined also with relatively low Fe concentrations in the latter two (Table 2).

Studies have shown that DOM has the potential to mobilise As from Fe oxides, probably as a result of competition of DOM and arsenate for sorption sites (Bauer and Blodau, 2006; Redman et al., 2002). This mechanism might increase the dissolved fraction of As and possibly also V and was not included in the modelling. This could lead to an overestimation of the adsorbed fraction in the present study.

On the other hand, adsorption to other additional phases, e.g. Mn or Al oxides was not considered in the present study. If additional adsorption phases had been included, a larger fraction of the arsenate might have been modelled as adsorbed in some streams.

The recent study of Sjöstedt et al. (2009) suggests that the former uncertainty may be more important as the use of a similar model slightly overestimated the binding of As to colloidal phases for the surface water of 3 lakes. Thus it seems possible that the colloidal

fractions as calculated in this study may also be slightly overestimated although the general pattern (i.e. strong colloidal binding) is likely to be correct. To provide more direct evidence it would be necessary to compare the modelled speciation with analytical speciation and/or ultrafiltration techniques for a number of streams used in this study.

It should also be kept in mind that the adsorption constants for vanadate used in the modelling in this study have been fitted from the results of one single study, which considered adsorption on Fe oxyhydroxide (Blackmore et al., 1996). The study included competitive adsorption by phosphate, while competitive adsorption with arsenate was not included. However, the adsorption constants found for vanadate are slightly higher compared to those for phosphate, indicating that vanadate is more strongly adsorbed to ferrihydrite than is phosphate. The adsorption constants for phosphate are in turn higher than the adsorption constants for arsenate included in the MINTEQ database, i.e the strength of the adsorption to ferrihydrite is assumed to increase in the order $\text{AsO}_4^{3-} < \text{PO}_4^{3-} < \text{VO}_4^{3-}$ (Table S1, online supplementary information). The relationship between adsorption constants for phosphate and arsenate is well established. It has for example been shown that phosphate suppresses As sorption by soils, in particular in soils with low amounts of Fe oxides (Smith et al., 2002). Vanadium has been less studied, but an earlier study indicated that vanadate should be more strongly adsorbed to Fe(hydr)oxides compared to arsenate (Rietra, 2001), which is consistent with the constants used here.

In the modelling, DOM was assumed to consist of 100 % fulvic acids. This may influence the possible amount of metals bound to DOM, since fulvic acids have a higher metal-binding capacity compared to humic acids (Milne et al., 2003). However, direct complexation of arsenate to DOM is generally considered negligible (Bauer and Blodau, 2006), while the extent of the complexation of vanadate to DOM is uncertain. Therefore complexation of arsenate and vanadate to DOM is not included in Visual MINTEQ. When V(IV) is present, it is modelled as entirely bound to DOM, however the V(IV) fraction can be considered as negligible according to the modelling results. Further, only a very small fraction of the Fe was modelled as bound to DOM. Therefore, the assumption that DOM is completely dominated by fulvic acids had only a minor, if any, impact on the modelling results.

Despite the model uncertainties, we believe that the modelling approach used gives reasonable results and thus a good indication of the speciation of As and V in Swedish rivers.

4.3. Temporal trends

Iron shows a general increasing trend in southern Sweden (Fig. 3). Neal et al. (2008) found increasing concentrations of Fe in UK upland waters, which they attributed to increasing DOC concentrations where their interpretation was that the organic matter stabilises micro-particulate precipitated Fe, by stabilising the colloids against aggregation. This mechanism has been shown in laboratory experiments using solutions similar to natural

water under circum-neutral pH (Tipping, 1981) and is thus also believed to be relevant in actual natural waters. This is a likely effect also in the present study, where Fe was mainly modelled as precipitated ferrihydrite (Table 2) and where general increasing trends were found for both Fe and TOC in southern Sweden (Fig. 3).

For both As and V, it has been shown that the atmospheric deposition is decreasing. Arsenic in precipitation has decreased significantly by about 50-60% between 1989-1998 in the south of Sweden (Kindbom et al., 2001), while concentrations of V in moss decreased by about 50% in southern and mid Sweden from 1970 to 1995 (Rühling and Tyler, 2001). An additional moss study in southern Sweden, in an area not affected by any major local sources, showed that concentrations of both As and V in moss decreased by slightly above 80% between 1975-2000 (Rühling and Tyler, 2004). Despite the significant decrease in atmospheric deposition, total concentrations of both As and V are generally increasing in stream water in southern Sweden, even though the increase is not always significant in each separate stream (Figs 4, 5a and 6a). This result suggests that atmospheric deposition is not the main influencing factor for concentrations of As and V in Swedish streams.

Trend analyses on the modelled fractions of As indicate that increasing total concentrations of As is often a result of an equal increase in the adsorbed concentration, but significant increases in the dissolved free concentration occur in some cases (Fig. 5). All streams that show a larger increase in the dissolved free fraction compared to the adsorbed fraction have a mean pH of 7 or higher and positive Theil's slope estimates for pH during the studied period (Table 1, Figs 3 and 5). There is also a relatively good correspondence ($r^2=0.32$, $p<0.001$) between trends in modelled adsorbed arsenate and particulate Fe, indicating that particulate Fe is important in determining As concentrations in the streams (Fig. 7a). This correlation is also significant using non-parametric correlation analyses ($p<0.0001$, Spearman R and Kendall Tau).

In laboratory experiments, the presence of dissolved organic matter caused the formation of As containing colloids by stabilizing fresh Fe-(oxy)hydroxides precipitates in solution (Ritter et al., 2006). Increased transport of As from soils in the drainage area and increasing mobility in the stream water as a result of increasing transport and stream water concentrations of DOC and Fe would be a likely explanation also for many of the increasing As trends in the present study.

For V, increasing total concentrations are almost entirely due to increasing concentrations of the adsorbed fraction, with virtually no influence of changes in the dissolved free fraction, according to the modelled speciation (Fig. 6). Further, trends for modelled particulate Fe and modelled adsorbed vanadate correspond well (Fig. 7b, $r^2=0.65$, $p<0.001$). This correlation is also significant using non-parametric correlation analyses ($p<0.0001$, Spearman R and Kendall Tau). Since the adsorbed fraction of V seems to be responsible for the entire increase in total V concentration, this indicates that transport with Fe determines the total

concentrations of V in Swedish streams. As a consequence the concentration of the free, potentially toxic, vanadate ion is normally very low in Swedish streams.

For As the picture is slightly more complicated. Transport with Fe particles also seems to be an important determining factor for As concentrations in Swedish streams, but increasing pH also seems to cause increased concentrations of the dissolved free fractions, especially in streams where pH is already neutral or slightly alkaline. While the modelling results indicate that the dissolved free, potentially toxic, fraction is normally very low in streams with $\text{pH} < 7$, it increases in streams with higher pH (Fig. 5).

5. Conclusions

A general trend of increasing concentrations of As and V in southern Swedish streams was detected and total concentrations of V were also found to increase slightly in the northern part of the country. Concentrations of As and V correlated significantly with Fe concentrations in almost all streams, indicating that Fe is an important determining factor for As and V concentrations in Swedish streams. This result was confirmed by the geochemical modelling which suggests that arsenate and vanadate adsorbed to oxides, e.g. ferrihydrite, are the dominating forms of As and V in Swedish streams and that the increasing concentrations are mainly due to an increase in the adsorbed fraction. This is most likely a result of increasing concentrations of colloidal Fe, probably stabilised by increasing concentrations of DOC. The modelling results further indicate that the dissolved fractions of As and V are generally small, with the exception of a few streams with high pH and/or PO_4^{3-} concentrations.

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Figure 1. Location of the 62 sampling sites throughout Sweden included in this study. The catchment areas are shown for 34 major rivers. For subcatchments of larger catchments and small catchments, only sampling points are indicated.

Figure 2. Correlation between measured concentrations of Fe, As and V for five selected streams with different sizes of drainage area (3-40157 km²) and pH (4.9-7.3). LogFe and logAs (left panel); logFe and logV (right panel). All correlations are significant ($p<0.001$). a) Torne älv; $r^2=0.54$ and 0.62 respectively b) Stormyrbäcken; $r^2=0.87$ and 0.74 c) Göta älv; $r^2=0.43$ and 0.91 d) Pipbäcken; $r^2=0.95$ and 0.94 e) Mörrumsån; $r^2=0.20$ and 0.85

Figure 3. Trends (Theil's slopes) for pH, TOC (mg L⁻¹ a⁻¹) and Fe (μg L⁻¹ a⁻¹). Significant trends (p < 0.05, Seasonal Kendall) are marked with darker coloured bars. The streams are sorted from north (top) to south. Numbers after the stream names indicate the first and last years of the time series, numbers in parenthesis indicate the number of samples included in the trend analysis.

Figure 4. Temporal trends of total concentrations of As (ng L^{-1} , left panel) and V (ng L^{-1} , right panel) in 9 selected streams in southern Sweden, all of which show significantly increasing As concentrations. The streams are sorted from north (top) to south. Trend lines are representations of the Theil's slopes. Non-significant positive Theil's slopes for V are indicated by dashed lines. In Motala ström, there is no detectable slope for V (no trendline). Note that the scale on the y-axis differ between the streams.

Figure 5. Trends (Theil’s slopes) for As (ng L⁻¹ a⁻¹). Total As concentration as well as the fractions of As modelled as adsorbed to Fe oxide (ferrihydrite) and dissolved free As (as arsenate). Significant trends (p<0.05, Seasonal Kendall) are marked with darker coloured bars. The streams are sorted from north (top) to south. Numbers after the stream names indicate the first and last years of the time series, numbers in parenthesis indicate the number of samples included in the trend analysis.

Figure 6. Trends (Theil's slopes) for V (ng L⁻¹ a⁻¹). Total V concentration as well as the fractions of V modelled as adsorbed to Fe oxide (ferrihydrite) and dissolved free V (as vanadate). Significant trends (p<0.05, Seasonal Kendall) are marked with darker coloured bars. The streams are sorted from north (top) to south. Numbers after the stream names indicate the first and last years of the time series, numbers in parenthesis indicate the number of samples included in the trend analysis.

a b
Figure 7. Correlation between trends of Fe_{part} ($\mu\text{g L}^{-1} \text{a}^{-1}$), As_{ads} ($\text{ng L}^{-1} \text{a}^{-1}$) and V_{ads} ($\text{ng L}^{-1} \text{a}^{-1}$).

Table 1

Features of the investigated streams, including sampling period, number of samples, drainage area, mean pH and mean total concentrations of ANC (Acid Neutralizing Capacity), TOC (Total Organic Carbon), Fe, As, V and DIP (inorganic P). The streams are sorted from north (top) to south and the page break divides the northern and southern streams.

Stream	dr area (km ²)	pH	ANC (meq L ⁻¹)	TOC (mg L ⁻¹)	Fe (µg L ⁻¹)	As (ng L ⁻¹)	V (ng L ⁻¹)	DIP (µg L ⁻¹)
Abiskojokk, 98-07 (107)	566	7.29	0.33	1.5	38	60	90	1.3
Killingi, 01-07 (81)	2347	6.83	0.24	2.3	233	50	100	2.9
Muddusälven, 01-07 (84)	452	7.04	0.28	5.3	1289	100	110	3.4
Övre Lansjärv, 01-07 (83)	1281	6.71	0.32	6.8	2211	180	460	24.8
Kukkasjärvi, 01-07 (83)	494	6.54	0.22	11.2	1303	290	520	6.0
Råne älv, 98-07 (120)	3781	6.72	0.22	7.3	1343	170	240	4.4
Torne älv, 98-07 (114)	40,157	6.84	0.28	6.5	831	120	420	6.5
Kalix älv, 98-07 (116)	18,081	6.83	0.28	4.7	859	120	290	5.1
Laxtjärnsbäcken, 01-07 (106)	11	6.84	0.18	3.6	331	90	90	2.8
Lule älv, 98-07 (106)	25,225	6.89	0.18	2.7	211	160	110	1.9
Pite älv, 98-07 (105)	11,285	6.81	0.19	3.7	379	220	190	3.3
Kvistforsen, 98-07 (86)	11,309	6.85	0.20	4.4	232	600	80	2.0
Vindelälven, 98-07 (105)	9827	6.96	0.24	3.9	226	460	80	2.2
Svarterget, 01-07 (81)	2	5.20	0.13	20.3	1258	550	670	11.6
Rickleån, 98-07 (116)	1648	6.68	0.21	11.5	595	890	320	4.7
Ume älv, 98-07 (113)	26,567	7.00	0.24	4.0	207	380	120	2.2
Lilltjärnsbäcken, 01-07 (110)	1	6.58	0.19	5.2	148	70	90	1.1
Öre älv, 98-07 (117)	2860	6.70	0.23	10.1	900	1270	400	5.3
Västersel, 01-07 (84)	1501	6.54	0.22	10.9	947	640	510	8.2
Ammerån, 98-07 (105)	2487	7.55	0.95	6.9	173	180	60	1.9
Gide älv, 98-07 (98)	3442	6.60	0.19	9.6	677	600	250	4.0
Ångermanälven, 98-07 (115)	30,639	6.94	0.24	5.2	202	200	100	2.0
Indalsälven, 98-07 (108)	25,765	7.28	0.42	4.3	81	150	90	1.8
Ljungan, 98-07 (106)	12,088	7.21	0.44	6.0	257	200	320	2.7
Stormyrbäcken, 01-07 (87)	3	6.50	0.27	8.8	1574	350	190	4.2
Delångersån, 98-07 (118)	1992	6.95	0.26	6.1	130	240	170	2.7
Ljusne Strömmar, 98-07 (117)	19,818	7.00	0.27	6.8	293	180	190	2.9
Lill-Fämtan, 01-07 (111)	6	4.89	0.03	10.0	421	200	490	2.8
Ö. Dalälven, 98-07 (114)	12,271	7.04	0.23	5.8	87	130	110	2.2
V. Dalälven, 98-07 (115)	8423	6.80	0.19	8.3	489	190	340	2.7

Stream	dr area (km ²)	pH	ANC (meq L ⁻¹)	TOC (mg L ⁻¹)	Fe (µg L ⁻¹)	As (ng L ⁻¹)	V (ng L ⁻¹)	DIP (µg L ⁻¹)
Klarälven, 01-07 (76)	8697	6.75	0.18	6.6	441	130	260	2.9
Kringlan, 01-07 (83)	294	6.71	0.22	10.1	434	290	370	3.6
Ringsmobäcken, 01-07 (87)	2	4.45	0.02	12.0	347	350	380	1.8
Kvarnebäcken, 02-07 (127)	7	5.16	0.05	10.1	454	320	370	2.0
Gullspångsälven, 98-07 (118)	5032	7.01	0.24	7.1	149	270	250	2.7
Enningsdalsälven, 98-07 (118)	624	6.78	0.18	8.0	191	340	380	3.1
Nyköpingsån, 98-07 (117)	3590	7.39	0.88	10.8	227	590	610	7.3
Kila, 01-07 (83)	140	6.68	0.38	11.2	835	550	490	6.1
Tidan, 98-07 (117)	2190	7.29	1.14	12.1	1212	530	1460	31.5
Lommabäcken, 01-07 (102)	1	4.45	0.02	14.9	497	380	430	3.2
Brätämsbäcken, 01-07 (80)	10	4.77	0.07	16.9	734	390	570	3.3
Dalbergsån, 98-07 (114)	832	6.95	0.55	10.9	886	530	1760	43.5
Motala Ström, 98-07 (118)	15,387	7.60	0.96	7.5	170	470	610	11.9
Örekilsälven, 98-07 (111)	1335	6.97	0.30	10.0	557	390	980	13.0
Lidan, 98-07 (119)	2263	7.66	2.33	13.6	1189	660	1430	41.5
Bäveån, 98-07 (118)	301	7.04	0.46	10.9	675	470	1050	12.3
Göta Älv, 98-07 (118)	46,886	7.27	0.33	4.5	130	220	320	3.3
Nossan, 98-07 (118)	811	7.33	1.04	13.7	1211	570	1530	43.8
Alelyckan, 98-07 (119)	48,193	7.23	0.33	4.6	284	300	640	6.1
Botorpström, 98-07 (118)	975	7.17	0.56	12.2	183	390	390	3.9
Emån, 98-07 (119)	4471	7.01	0.52	12.8	664	400	550	18.4
Pipbäcken, 01-07 (106)	3	4.86	0.03	10.8	1991	500	530	3.4
Ätran, 98-07 (112)	3340	7.06	0.46	9.7	702	410	620	6.3
Nissan, 98-07 (115)	2677	6.76	0.35	13.7	1238	500	790	6.4
Ljungbyån, 98-07 (117)	735	6.77	0.48	15.1	852	480	750	7.8
Lagan, 98-07 (113)	6095	6.73	0.28	12.0	968	390	600	4.3
Lyckebyån, 98-07 (117)	810	6.77	0.36	16.8	1689	530	970	6.0
Mörumsån, 98-07 (113)	3365	6.98	0.29	12.0	503	420	560	4.0
Rönneån, 98-07 (114)	970	7.56	1.43	10.5	747	510	1060	13.1
Råån, 98-07 (116)	166	7.88	4.10	4.7	414	640	980	66.9
Helgeån, 98-07 (119)	4144	7.17	0.58	15.6	1933	630	1270	8.6
Kävlingeån, 98-07 (118)	1185	7.81	3.34	8.1	295	1160	830	43.9

Table 2

Modelling results (mean values). Fraction % of the Fe modelled as particulate fraction (ferrihydrite) and fractions (%) of arsenate and vanadate modelled as adsorbed to ferrihydrite. The streams are sorted from north (top) to south and the page break divides the northern and southern streams.

Stream	Fe _{part} (%)	As _{ads} (%)	V _{ads} (%)
Abiskojokk, 98-07 (107)	100	43	56
Killingi, 01-07 (81)	100	96	97
Muddusälven, 01-07 (84)	100	100	100
Övre Lansjärv, 01-07 (83)	100	100	100
Kukkasjärvi, 01-07 (83)	100	100	100
Råne älv, 98-07 (120)	100	100	100
Torne älv, 98-07 (114)	100	99	99
Kalix älv, 98-07 (116)	100	100	100
Laxtjärnsbäcken, 01-07 (106)	100	98	99
Lule älv, 98-07 (106)	100	98	98
Pite älv, 98-07 (105)	100	99	99
Kvistforsen, 98-07 (86)	100	99	99
Vindelälven, 98-07 (105)	100	95	96
Svartberget, 01-07 (81)	94	99	100
Rickleån, 98-07 (116)	100	100	100
Ume älv, 98-07 (113)	100	97	97
Lilltjärnsbäcken, 01-07 (110)	99	99	99
Öre älv, 98-07 (117)	100	100	100
Västersel, 01-07 (84)	100	99	99
Ammerån, 98-07 (105)	100	88	93
Gide älv, 98-07 (98)	100	100	100
Ångermanälven, 98-07 (115)	100	98	98
Indalsälven, 98-07 (108)	100	69	78
Ljungan, 98-07 (106)	100	77	84
Stormyrbäcken, 01-07 (87)	100	100	100
Delångersån, 98-07 (118)	99	85	89
Ljusne Strömmar, 98-07 (117)	100	98	98
Lill-Fämtan, 01-07 (111)	92	99	100
Ö. Dalälven, 98-07 (114)	99	76	83
V. Dalälven, 98-07 (115)	100	100	100

Stream	Fe _{part} (%)	As _{ads} (%)	V _{ads} (%)
Klarälven, 01-07 (76)	100	100	100
Kringlan, 01-07 (83)	100	100	100
Ringsmobäcken, 01-07 (87)	83	97	99
Kvarnebäcken, 02-07 (127)	96	100	100
Gullspångsälven, 98-07 (118)	100	91	94
Enningsdalsälven, 98-07 (118)	99	96	97
Nyköpingsån, 98-07 (117)	100	61	77
Kila, 01-07 (83)	100	100	100
Tidan, 98-07 (117)	100	85	94
Lommabäcken, 01-07 (102)	85	97	99
Brätämsbäcken, 01-07 (80)	93	99	100
Dalbergsån, 98-07 (114)	100	59	82
Motala Ström, 98-07 (118)	100	36	59
Örekilsälven, 98-07 (111)	100	93	96
Lidan, 98-07 (119)	100	64	86
Bäveån, 98-07 (118)	100	96	97
Göta Älv, 98-07 (118)	100	66	79
Nossan, 98-07 (118)	100	69	88
Alelyckan, 98-07 (119)	100	85	92
Botorpström, 98-07 (118)	100	84	90
Emån, 98-07 (119)	100	84	92
Pipbäcken, 01-07 (106)	97	100	100
Ätran, 98-07 (112)	100	98	99
Nissan, 98-07 (115)	100	100	100
Ljungbyån, 98-07 (117)	100	98	99
Lagan, 98-07 (113)	100	100	100
Lyckebyån, 98-07 (117)	100	100	100
Mörrumsån, 98-07 (113)	100	100	100
Rönneån, 98-07 (114)	100	89	95
Råån, 98-07 (116)	100	13	46
Helgeån, 98-07 (119)	100	100	100
Kävlingeån, 98-07 (118)	100	17	46

Supplementary information

Figure S1. Performance of the estimated adsorption constant for adsorption of vanadate to iron. Iron concentration (as iron hydroxide): 10^{-2} or 10^{-3} M. Initial vanadate concentration: 10^{-4} M. Lab results (black), redrawn from Blackmore et al. (1996). Modelling results (grey) using Visual Minteq and the new fitted adsorption constants.

Figure S2. Performance of the estimated adsorption constant for adsorption of vanadate to iron with (unfilled symbols) and without (filled symbols) presence of phosphate (10^{-4} M). Iron concentration (as iron hydroxide); 10^{-2} , 10^{-3} or 10^{-4} M. Initial vanadate concentration: 10^{-4} M. Lab results (black), redrawn from Blackmore, et al. (1996). Modelling results (grey) using Visual Minteq and the new fitted adsorption constants.

Figure S3. Performance of the estimated adsorption constant for adsorption of vanadate to iron in competition with phosphate (10^{-4} M). Iron concentration (as iron hydroxide); 10^{-2} , 10^{-3} or 10^{-4} M. Initial vanadate concentration: 10^{-4} M. Lab results (black), redrawn from Blackmore, et al. (1996). Modelling results (grey) using Visual Minteq and the new fitted adsorption constants.

Table S1. Adsorption constants for arsenate, phosphate and vanadate to ferrihydrite used in the modelling in the present study.

Adsorption reaction	Adsorption constants		
	M = As	M = P	M = V
$=\text{SOH} + \text{MO}_4^{3-} + 3\text{H}^+ = \text{SH}_2\text{MO}_4 + \text{H}_2\text{O}$	30.98	32.08	34.2
$=\text{SOH} + \text{MO}_4^{3-} + 2\text{H}^+ = \text{SHMO}_4^- + \text{H}_2\text{O}$	25.84	26.39	28.0
$=\text{SOH} + \text{MO}_4^{3-} + \text{H}^+ = \text{SMO}_4^{2-} + \text{H}_2\text{O}$	19.5	20.73	20.8

Reference

Blackmore, D.P.T., Ellis, J., Riley, P.J., 1996. Treatment of a vanadium-containing effluent by adsorption/coprecipitation with iron oxyhydroxide. *Water Research* 30, 2512-2516.