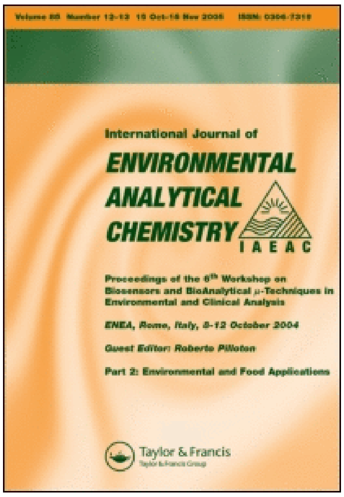


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# The Cumulation of Chromium and Arsenic Species in Fish (Poecilia reticulata)

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# The Cumulation of Chromium and Arsenic Species in Fish (Poecilia reticulata)

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Chromium-51 and arsenic-74 were used for the investigation of the uptake and the release of different chromium and arsenic species in fish. It has been found that only trimethylarsine can be rapidly taken up directly from water. The release of chromium(III), consumed by fish in food, is very rapid: about 99.9% of chromium is released within a few days. The same results were obtained with chromium(III) acetylacetonate or chromium(III) ethylenediaminotetraacetate. About 95% of arsenic acid, methylarsonic acid, dimethylarsinic acid or arsenic(III) diethyldithiocarbamate are released within a few days whereas the remaining arsenic is released with the biological half time $35 \pm 5$ days.

KEY WORDS: Chromium, arsenic, methylarsonic acid, dimethylarsinic acid, trimethylarsine, fish, Poecilia reticulata.



## INTRODUCTION

In our previous papers the cumulation and the release of methylmercury,[1] phenylmercury and inorganic mercury,[2] zinc and cadmium[3] in fish (Poecilia reticulata) has been investigated. In the continuation of these studies the uptake of chromium(III) and (VI), arsenic(III) and (V), methylarsonic acid, dimethylarsinic acid and trimethylarsine (organic arsenic was found in natural waters in significant concentrations because of the ability of phytoplankton to reduce and methylate arsenic(V))[4–6] by fish directly from water or sorbed on food has been studied in order to compare the cumulation of different species studied.

## EXPERIMENTAL

### Reagents and apparatus

Unless otherwise stated, all reagents were of analytical reagent grade purity.

Chromium-51 (2,000 GBq/g Cr, Amersham, England) and arsenic-74 (carrier-free, Amersham, England) were used for the preparation of labelled compounds. Chromium(III) acetylacetonate and chromium(III) ethylenediaminotetraacetate were prepared by boiling of chromium(III) solution with an excess of reagents. Arsenic(III) diethyldithiocarbamate was prepared by the extraction of arsenic-74 into carbon tetrachloride using an excess of sodium diethyldithiocarbamate. Labelled methylarsonic acid $CH_3{}^{74}AsO(OH)_2$, methylarsonous acid $CH_3{}^{74}As(OH)_2$ or methylarsinoxide $CH_3{}^{74}AsO$, dimethylarsinic (cacodylic) acid $(CH_3)_2{}^{74}AsO(OH)$, dimethylarsinous acid $(CH_3)_2{}^{74}As(OH)$ and trimethylarsine $(CH_3)_3{}^{74}As$ were prepared and purified according to paper.[7]

Labelled fish food was prepared in a similar manner as given in previous papers.[1-3] The attempts to prepare food containing chromium(VI), arsenic(III) and trimethylarsine were unsuccessful. Drying at room temperature led to the reduction of chromium(VI) and to the oxidation of arsenic(III); most of trimethylarsine was evaporated during drying even using complex $(CH_3)_3As.HgCl_2$.

The scintillation crystal NaI(Tl) was used for the radioactivity measurements.



### Procedures

The uptake of species investigated from water as well as sorbed on food and the release has been studied at 22°C in a similar manner as described earlier.[1-3] Samples of water and fish food were analysed during the experiment for the equilibrium concentration of chromium(III) and (VI),[8] the content of arsenic(III) and (V), methylarsonic acid, dimethylarsinic acid and trimethylarsine was determined according to the procedure given in paper.[7]

## RESULTS AND DISCUSSION

### Uptake of chromium from water

Fish kept in labelled chromium(III) solutions ($5 \times 10^{-8}$ mol.L$^{-1}$ and $2 \times 10^{-7}$ mol.L$^{-1}$) showed after 1–2 hours an appreciable radioactivity which was caused mostly by the sorption of chromium(III) on the surface of the fish. Using longer exposition time, the radioactivity of the fish increased relatively slow. From the results obtained it can be concluded that the cumulation of chromium(III) directly from water is low; the cumulation constant $K_w$ is lower than 2 days$^{-1}$ which means that after one day of the exposition the concentration of chromium in fish, $c_f$, is lower than $2c_{Cr}$ ($c_{Cr}$ denotes the concentration of chromium in water). When these fishes were transferred into non-active water the radioactivity decreased with a half-time $8 \pm 2$ days (mean from ten fishes). From the theory[9] it follows that the maximum concentration of chromium in fish, taken up directly from water, is lower than $10c_{Cr}$.

Fish kept in labelled chromium(VI) solutions ($10^{-7}$ mol.L$^{-1}$ and $2 \times 10^{-7}$ mol.L$^{-1}$) showed after a short exposition time only low radioactivity (the sorption of chromium(VI) on the surface of the fish is small). The exact value of the cumulation constant ($K_w < 1$ day$^{-1}$) cannot be determined because after longer exposition time chromium(VI) was reduced to chromium(III). The biological half-time was found to be $15 \pm 5$ days.



## Uptake of chromium species from food

Fish fed by food labelled with chromium(III) showed a very rapid decrease of the radioactivity. After four days about 99.9% of chromium was released: biological half-time was $0.3 \pm 0.1$ days (mean from 12 samples). The remaining radioactivity was released with a half-time $15 \pm 4$ days (see Fig. 1).

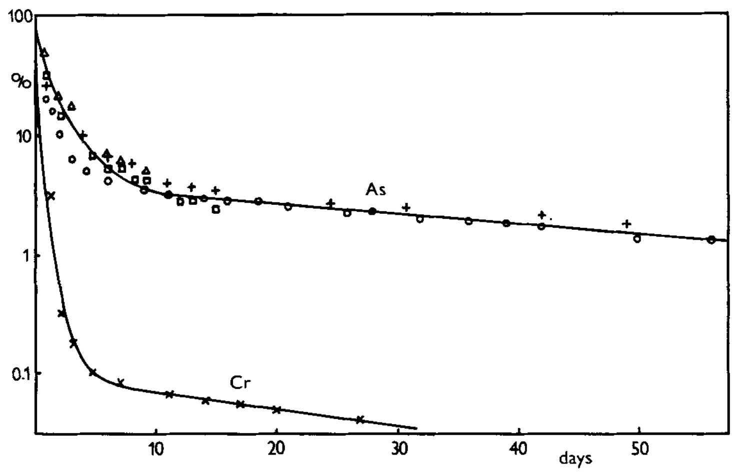


FIGURE 1 The release of arsenic acid (○), arsenic(III) diethyldithiocarbamate (+), methylarsonic acid (△), dimethylarsinic acid (□) and chromium(III) (×) after a short time feeding.

The concentration of chromium in fish, taken up from food, can be expressed as follows[9]

$$c_f = 0.999\frac{K_m c'_{Cr}}{2.3}(1 - e^{-2.3t}) + 0.001\frac{K_m c'_{Cr}}{0.046}(1 - e^{-0.046t}) \quad (1)$$

where $K_m$ denotes the mean weight of food (in g) consumed daily per g of fish, $c'_{Cr}$ is the concentration of chromium in food, $t$ is the time of the exposition (in days).

From the above equation it follows that the maximum concentration of chromium in fish is $0.45\,K_m c'_{Cr}$.

## Uptake of arsenic species from water

Fish kept in labelled arsenic acid ($3 \times 10^{-8}$ mol.L$^{-1}$ and $10^{-7}$ mol.L$^{-1}$), methylarsonic acid ($10^{-8}$ mol.L$^{-1}$) and dimethylarsinic acid ($10^{-5}$ mol.L$^{-1}$) showed even after several days only negligible radioactivity; the cumulation constant $K_w$ was lower than 0.03 days$^{-1}$ (mean from 10 fishes). The uptake of labelled arsenic trioxide, methylarsonous acid and dimethylarsinous acid directly from water was also low. However, it should be noted that these species present in low concentrations were gradually oxidized in water by air oxygen. Some experiments with $10^{-5}$ M arsenic(III) solutions showed that the $K_w$ value was lower than 0.1 days$^{-1}$.

It has been found that only trimethylarsine can be rapidly taken up by fish. The exact value of $K_w$ cannot be determined because only short exposition time (up to 30 min) can be used: trimethylarsine volatilized and it is oxidized in aqueous solutions (the uptake of the oxidation products was found to be also low); moreover, the cumulation is complicated by the sorption of trimethylarsine on the surface of the fish. The complex $(CH_3)_3As.HgCl_2$ is more stable against oxidation; fish kept in $10^{-7}$ M $(CH_3)_3As.HgCl_2$ cumulated arsenic with $K_w = 2-10$ days$^{-1}$. If trimethylarsine is liberated from the complex by the addition of zinc powder or an excess of potassium iodide the cumulation constant is at least one order higher.

## Uptake of arsenic species from food

It has been found that about 95% of arsenic(V), consumed by fish in food, was released with the half-time $0.3 \pm 0.1$ days (mean from 15 fishes). The remaining activity decreased with the half-time $35 \pm 5$ days (see Fig. 1).

The concentration of arsenic in fish can be expressed according to[9]

$$c_f = 0.95\frac{K_m c'_{As}}{2.3}(1 - e^{-2.3t}) + 0.05\frac{K_m c'_{As}}{0.02}(1 - e^{-0.02t}) \qquad (2)$$

where $c'_{As}$ denotes the concentration of arsenic in food.

The maximum concentration of arsenic in fish, taken up from food, equals to about $3\,K_m c'_{As}$.

Practically the same results were obtained using labelled with arsenic(III) diethyldithiocarbamate, methylarsonic acid and dimethylarsinic acid (see Fig. 1).

## CONCLUSION

The following conclusions can be made from the present as well as from previous papers:[1-3]

1) Only methylmercury chloride ($K_w = 237 \pm 67$ days$^{-1}$), phenylmercury chloride($K_w = 212 \pm 49$ days$^{-1}$) and trimethylarsine (to some extent also mercury(II) chloride) are cumulated rapidly by fish directly from water. Chromium(III), zinc and cadmium are cumulated in a low extent ($K_w < 1$–$2$ days$^{-1}$), whereas only negligible uptake has been observed in the case of arsenic(III) and (V), methylarsonic acid and dimethylarsinic acid.

2) The cumulation of toxic elements taken up by fish from food decreases in the following order (the maximum concentration of species is given in brackets): methylmercury chloride ($160\,K_m c'_M$), phenylmercury chloride ($26\,K_m c'_M$), inorganic mercury(II), ($7\,K_m c'_M$), zinc ($6\,K_m c'_M$), arsenic acid, methylarsonic acid and dimethylarsinic acid ($3\,K_m c'_M$) cadmium ($1.1\,K_m c'_M$) and chromium(III) ($0.45\,K_m c'_M$).



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