

## Geomorphology, hydrology, and the bioavailability of mercury to riverine food webs

### Géomorphologie, hydrologie et biodisponibilité du mercure dans les réseaux trophiques fluviaux

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## RÉSUMÉ

Le Yuba Fan dans les contreforts de la Sierra Nevada en Californie est un site emblématique de terrain en géomorphologie parce que c'est un vestige évident de l'époque des exploitations aurifères hydrauliques à grande échelle du 19<sup>ème</sup> siècle et parce qu'il a été bien étudié et documenté au début du 20<sup>e</sup> siècle par GK Gilbert. Il a été constitué par le déplacement de  $\sim 250 \times 10^6 \text{ m}^3$  de sédiments. Cet article revisite ce site classique sur le terrain pour évaluer ce qui s'est passé depuis la rédaction de l'ouvrage classique de Gilbert et réévaluer l'héritage toxique de l'exploitation minière de l'or. Le mercure était utilisé pour l'amalgame et environ  $4 \times 10^6 \text{ kg}$  de mercure ont été perdus lors du processus d'exploitation minière. Ce mercure s'est largement mélangé avec des sédiments déplacés, donc la concentration de mercure est indicative des processus d'évolution du Yuba Fan. Nous démontrons que le Yuba Fan libère encore activement des sédiments chargés de mercure du piémont de la vallée centrale de Californie lors d'inondations qui ont lieu une fois tous les dix ans, capables de produire une érosion des berges et des terrasses le long de la rivière Yuba, et qui sont de plus en plus fréquentes en raison des changements climatiques. Ces sédiments transportés posent alors des risques majeurs de contamination pour les écosystèmes en aval composés de poissons migrateurs et d'oiseaux. Notre analyse comprend une évaluation de la biodisponibilité du mercure, et enquête sur les contrôles physiques et chimiques, sur la manière et le lieu où le mercure est transformé en méthylmercure et devient disponible pour entrer dans les réseaux trophiques régionaux.

## ABSTRACT

The Yuba Fan in the Sierra Nevada foothills of California is an iconic field site in geomorphology because it is a visible legacy of the extensive 19<sup>th</sup> Century hydraulic gold mining and because it was well studied and documented in the early 20<sup>th</sup> Century by G.K. Gilbert. It was formed by the displacement of  $\sim 250 \times 10^6 \text{ m}^3$  of sediment. This paper revisits this classic field site to assess what has happened since Gilbert's classic work and to re-evaluate the toxic legacy of gold mining. Mercury was used to amalgamate and an estimated  $4 \times 10^6 \text{ kg}$  of Hg was lost to the mining process. This mercury largely mixed in with displaced sediment, so Hg concentration is indicative of the processes of fan evolution. We demonstrate that the Yuba Fan still actively releases Hg-laden sediment from the piedmont to the Central Valley of California during once-a-decade flood events that are capable of producing bank/terrace erosion along the Yuba River, and which are increasingly common due to climate changes. This transported sediment then poses major contamination risks to downstream ecosystems comprised of migratory fish and birds. Our analysis includes an assessment of the bioavailability of Hg, which investigates the physical/chemical controls on how and where Hg is transformed to methylmercury and therefore becomes available to enter regional food webs.

## KEYWORDS

Bioavailability, chemical speciation, complexation, anthropogenic effects, floods, modeling.

## **GEOMORPHOLOGY, HYDROLOGY, AND THE BIOAVAILABILITY OF MERCURY TO RIVERINE FOOD WEBS**

The interrelationships between hydrologically driven evolution of legacy landscapes downstream of major mining districts and the contamination of lowland ecosystems are poorly understood over centennial time scales. Here, we demonstrate within piedmont valleys of California's Sierra Nevada, through new and historical data supported by modeling, that anthropogenic fans produced by 19th century gold mining comprise an episodically persistent source of sediment-adsorbed Hg to lowlands. Within the enormous, iconic Yuba Fan, we highlight (i) an apparent shift in the relative processes of fan evolution from gradual vertical channel entrenchment to punctuated lateral erosion of fan terraces, thus enabling entrainment of large volumes of Hg-laden sediment during individual floods, and (ii) systematic intrafan redistribution and downstream progradation of fan sediment into the Central Valley, triggered by terrace erosion during increasingly long, 10-y flood events. Each major flood apparently erodes stored sediment and delivers to sensitive lowlands the equivalent of ~10–30% of the entire postmining Sierran Hg mass so far conveyed to the San Francisco Bay-Delta (SFBD). This process of protracted but episodic erosion of legacy sediment and associated Hg is likely to persist for >104 y. It creates, within an immense swath of river corridor well upstream of the SFBD, new contaminated floodplain surfaces primed for Hg methylation and augments/replenishes potential Hg sources to the SFBD. Anticipation, prediction, and management of toxic sediment delivery, and corresponding risks to lowland ecology and human society globally, depend on the morphodynamic stage of anthropogenic fan evolution, synergistically coupled to changing frequency of and duration extreme floods.

Bioavailability of sediment-adsorbed contaminants to food webs in river corridors is typically controlled by biological, chemical, and physical factors, but understanding of their respective influences is limited due to a dearth of landscape-scale investigations of these biogeochemical links. Studies that account for the dynamics and interactions of hydrology and sediment transport in affecting the reactivity of sediment-adsorbed heavy metals such as mercury (Hg) are particularly lacking. Sequences of flood events generate complex inundation histories with banks, terraces, and floodplains that have the potential to alter local redox conditions and thereby affect the oxidation of elemental Hg<sup>0</sup> to inorganic Hg(II), and the microbial conversion of Hg(II) to methylmercury (MeHg), potentially increasing the risk of Hg uptake into aquatic food webs. However, the probability distributions of saturation/inundation frequency and duration are typically unknown for channel boundaries along sediment transport pathways, and landscape-scale characterizations of Hg reactivity are rare along contaminated rivers.

This research provides the first links between the dynamics of physical processes and biochemical processing and uptake into food webs in fluvial systems beset by large-scale mining contamination. Here we present new research on Hg-contaminated legacy terraces and banks along the Yuba River anthropogenic fan, produced by 19th C. hydraulic gold mining in Northern California. To assess the changes in Hg(II) availability for methylation and MeHg bioavailability into the food web, we combine numerical modeling of streamflow with geochemical assays of total Hg and Hg reactivity to identify hot spots of toxicity within the river corridor as a function of cycles of wetting/drying. We employ a 3D hydraulic model to route historical streamflow hydrographs from major flood events through the Yuba and Feather Rivers into the Central Valley to assess the frequency and duration of saturation/inundation of channel boundary sediments. We compare these spatiotemporal modeling results to sediment total Hg and stannous chloride 'reducible' Hg(II) concentrations (the latter as a proxy for Hg(II) availability for methylation) along this ~70 km swath of river corridor. Finally, we evaluate these potential hot spots of Hg toxicity against MeHg concentrations in local aquatic biota at several trophic levels. The research will provide the basis for new models describing the evolution of toxic substances in river corridors and may prove helpful in explaining the contribution of Hg to food webs of the San Francisco Bay-Delta as an enduring legacy of California's 19th C. Gold Rush.



Photograph of failing contaminated terraces in upper Yuba Fan.

## LIST OF REFERENCES

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