

EFFECTS OF SUSPENDED SOLIDS AND DISSOLVED ORGANIC CARBON ON NICKEL TOXICITY

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Abstract—Nickel (Ni) is a common and potentially toxic heavy metal in many fluvial ecosystems. We examined the potentially competitive and complementary roles of suspended sediment and a dissolved organic ligand, humate, in affecting the partitioning and toxicity of Ni to a model organism, *Daphnia magna*, in both batch and stream-recirculating flume (SRF) tests. Sediments included a fine-grained deposit, montmorillonite, and kaolinite. Survival of *D. magna* was unaffected by the range of suspended solids used in the present study (8–249 mg/L). However, exposure to suspended solids that were amended with Ni had a deleterious effect on test organism survival, which is attributed to partitioning of Ni into the aqueous phase. At comparable levels of dissolved Ni, survival of *D. magna* was reduced in tests with Ni-amended suspended solids compared to Ni-only aqueous exposures, suggesting potentiation between these two aquatic contaminants. Addition of humate attenuated toxicity to *D. magna* in both Ni-only and Ni-amended suspended sediment exposures. These results indicate that organic ligands and suspended solids have important functions in affecting the bioavailability and toxicity of Ni to aquatic organisms and should be incorporated into predictive models to protect ecosystem quality. Environ. Toxicol. Chem. 2010;29:1781–1787. © 2010 SETAC

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INTRODUCTION

Nickel (Ni) is abundant in the Earth's crust [1], and with many industrial and commercial uses, contamination of surface waters is ubiquitous in human-dominated watersheds [2–3]. The bioavailability and toxicity of Ni in aquatic systems ([4–6]; <http://www.atsdr.cdc.gov/toxprofiles/tp15-c6.pdf>) are often determined by sorption to solid phases [7] and complexation with dissolved ligands, particularly dissolved organic matter (DOM) [8,9]. These reactions affect the amount of total Ni in solution and reduce the fraction as free ionic Ni (Ni^{2+}), which, for many organisms, is presumed to be the toxic metal species [10–16]. Sorption of free ionic and complexed Ni species to solid phases occurs through processes of ligand binding and hydrophobic [17] and electrostatic attraction [18]. This results in Ni being associated with a variety of natural solid phases, including, for example, organic matter, metal oxyhydroxides, and clays [19,20]. The affinity of aqueous Ni for particles is often expressed as the distribution coefficient (K_d , L/kg), which is the ratio of measured concentration on the solid phase to that in the enveloping aqueous phase [21].

Suspended solids (SS) can reduce dissolved metal concentrations and thereby potentially ameliorate toxicity, but also may adversely impact aquatic biota. Indeed, SS, rather than metals or nutrients, have been identified as the most common cause of river and stream impairment [6,22]. Hence, while extreme loadings of suspended sediments can be toxic to aquatic biota, moderate levels of SS, through their sorptive affinity for dissolved metals, may attenuate bioavailability and toxicity of co-occurring metal contaminants such as Ni.

Humic substances are ubiquitous components of DOM in natural waters and have important roles in both mitigating metal toxicity to aquatic organisms [9,23] and affecting partitioning of metals between aqueous and solid phases. Humic substances contain a range of chelating functional groups (carboxyl, thiol) that serve to reduce free metal ion concentration and bioavailability. Moreover, the rate and extent of metal adsorption to particles is dependent on the concentration and quality of DOM [8,9,24,25], which competes with solid-phase ligands for metals. Adsorption of metal ions to surfaces of clay minerals, for example, decreases in the presence of dissolved organic ligands [26]. Toxicity is defined as accumulation of metal at the biotic ligand at or above a critical threshold concentration [27].

Here we examine the potentially competitive and complementary roles of suspended sediment and humic substances in affecting the partitioning and toxicity of Ni to a model test organism, *Daphnia magna*. In a recent literature search, Meyer et al. [10] found no Ni toxicity tests in which only SS was varied. Further, there is limited information on the effect of DOM on Ni toxicity [12,14]. With controlled, multivariate laboratory tests, we attempt to isolate natural (suspended sediment) and anthropogenic (nickel) stressors and predict their relative importance to aquatic biota.

MATERIALS AND METHODS

The effects of SS and a humic substance on Ni partitioning and toxicity to *D. magna* were investigated with a series of laboratory tests conducted with both batch and stream-recirculating flume (SRF) approaches. These experiments included examinations of single stressors (Ni only), different suspended particle types (natural sediment and two types of pure clays) and concentrations, with and without added Ni, and

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combinations of multiple variables (aqueous Ni + suspended particles + humate).

Test sediment

The effect of suspended sediments on partitioning and toxicity of Ni to *D. magna* was examined with a natural sediment and two clays, montmorillonite and kaolinite. Natural sediment was obtained following U.S. Environmental Protection Agency (U.S. EPA) protocols [28,29] from Warden Ditch Canal located in Clark County, Ohio, USA. This fine-grained (75% clay) and relatively high-organic content (7.7% total organic carbon) deposit had the following physicochemical characteristics (dry wt basis): total Ni = 18 mg/kg, simultaneously extracted metal (SEM) Ni = 6 mg/kg, acid volatile sulfides (AVS) = 2,500 mg/kg, total iron = 21 g/kg, total manganese = 410 mg/kg, SEM/AVS molar ratio = 0.001, water content = 76.4%, and pore water dissolved organic carbon (DOC) = 5.2 mg/L. Kaolinite (analytical grade, Fluka) was selected because it is a simple type of clay and a common, naturally occurring colloid [30]. In contrast, montmorillonite (KSF, analytical grade, Acros Organics) is a 2:1 layer mineral (smectite family) with a surface area five times greater than that of kaolinite. Montmorillonite has high cation-exchange capacity (CEC) due to substitution of the main cations with those having lower valence [26], which allows the mineral to bind not only free cations such as Ni but also organically complexed cations [30].

Warden Ditch sediment and the two clays were amended with Ni to a nominal concentration of 5,000 mg/kg dry weight. Concentrated stock solutions of Ni were prepared by dissolving NiCl₂·6H₂O in reagent-grade water (nominal resistivity, >15 MΩ-cm). Nickel stock solution was added to Warden Ditch deposits and aqueous slurries of pure kaolinite and montmorillonite in 4-L plastic bottles, homogenized for 2 h on a roller mill, and allowed to equilibrate for 56 d in the dark at 4°C [29]. Prior to the start of each test, containers of sediment and clay were rolled for another 2 h to incorporate any interstitial water that separated during storage. Nickel-spiked sediment/clay was added to test containers immediately after mixing. Sediment suspensions having 12.5, 25, and 50 nephelometric turbidity units (NTU) were prepared for each of the three Ni-amended solids and maintained in each beaker by magnetic stirring with a Teflon-coated bar (375 rpm). Monitoring of turbidity levels throughout the course of the experiments indicated that the suspensions were uniform.

Test conditions

Batch tests were conducted in 4-L glass beakers filled with culture water that was stirred magnetically. Stream-recirculating flume tests were conducted inside a fiberglass flume (Frigid Units[®]) in the laboratory. Water hardness in both batch and SRF experiments was prepared to replicate the 50th percentile of observed hardness in European surface waters (99 mg/L as CaCO₃). Test water was made by dissolving salts in reagent-grade water (adapted from Smith et al. [31]). Measured hardness of test water was 100 ± 5 mg/L as CaCO₃.

Daphnia magna test organisms were obtained from a culture in the Burton Laboratory at Wright State University, Dayton, Ohio, USA. These organisms were cultured from parental organisms, provided by the U.S. EPA, according to standard protocols in synthetic hard water (≈160–180 mg/L as CaCO₃) [31]. *Daphnia magna* used for laboratory tests were neonates (<24 h old, broods 2–5). Mortality was the acute endpoint; survival was determined by counting the number of living versus dead organisms (evaluated as immobility) at the end of each 48-h test.

In both batch and SRF tests *D. magna* were exposed to Ni and other stressors inside cylindrical chambers constructed of transparent cellulose acetate butyrate (10 *D. magna* neonates per chamber). Each chamber (7.0 cm outer diameter (OD), 6.7 cm inner diameter (ID), 13 cm long) had two rectangular windows (4 × 8 cm), covered with 250 μm nylon mesh, on opposite sides of the tube, and was closed on both ends with polyethylene caps [32]. Chambers were either suspended vertically inside 4-L glass beakers during batch experiments (one chamber per beaker) or secured horizontally to a plastic frame during flume tests (Cloran CE, 2008, Master's thesis, Wright State University, Dayton, OH, USA). Batch and SRF tests were conducted with a photoperiod of 16:8 h light:dark at 1.464 W m⁻² from a halogen lamp, as recommended by the U.S. EPA [28]. Organisms were deprived of food for the duration of the experiment.

Batch tests

Dynamic, nonrenewal, short-term batch tests were used to investigate Ni partitioning and the independent and interactive effects of multiple treatment variables on toxicity to *D. magna*. Levels of Ni and humate (humic acid, Sigma-Aldrich), a model Ni-complexing ligand, were varied in some batch tests, often in combination with each other and varying types (Warden Ditch sediment, montmorillonite, kaolinite) and amounts of suspended material. For batch tests (31 total), four replicates of each of the following treatments were conducted concurrently: Aqueous Ni only: Total dissolved Ni (measured) of 210, 350, 750, 1,500, 3,100, and 6,200 μg/L; Humate only: Humate concentrations of 1, 7, 18, 48, and 80 mg C/L (measured) were selected to reflect the natural range of DOC in most freshwater systems (≈1–15 mg C/L), although levels can vary seasonally by 10²-fold in some rivers [33,34]; Humate + aqueous Ni: Humate at 1, 7, 18, 48, 80 mg C/L in combination with the LC75 of Ni (lethal concentration of Ni for 75% of test organisms), as determined from Ni only tests; Suspended sediment only: Warden Ditch sediment, montmorillonite, and kaolinite at 50 NTU; Ni-amended suspended sediment only: Warden Ditch sediment (5,300 mg Ni/kg dry wt), montmorillonite (4,100 mg/kg), and kaolinite (3,600 mg/kg) at each of three turbidity levels (12.5, 25, and 50 NTU); Ni-amended suspended sediment + humate: Humate concentration of 7 mg C/L with either Ni-amended Warden Ditch sediment or montmorillonite clay at about 50 NTU; and control: Test water with no added Ni, suspended sediment, or humate.

Physicochemical parameters, including temperature, pH, dissolved oxygen, and conductivity, were measured electrochemically in each beaker at the start and end of each 48-h test. Hardness and alkalinity were determined with standard methods [35]. Physicochemical water quality variables were similar in all batch and SRF experiments (Table 1). Water samples also were collected from each chamber for analysis of total Ni and DOC in filtered water (0.4 μm, polycarbonate filter) and total Ni in unfiltered aliquots. Water for Ni analysis was sampled at the start and end of each 48-h test, with the exception of Ni-only treatments, which were sampled only at the start. Standard methods were used to determine total suspended solids (TSS) from a separate aliquot of test water [35]. Water for determination of Ni was acidified to 1% with HNO₃ (J.T. Baker Instra-Analyzed[®]) and water for DOC analysis was acidified to 1% with HCl and stored refrigerated.

SRF tests

Daphnia magna were exposed to Ni in chambers inside a recirculating stream channel (inner dimensions, 2.9 m

Table 1. Mean (± 1 standard deviation of the mean) physicochemical characteristics of test water for 31 batch and three stream-recirculating flume (SRF) experiments

Test type	pH	Temperature (°C)	Dissolved O ₂ (mg/L)	Specific conductance (μ S/cm)	Hardness (mg/L as CaCO ₃)	Alkalinity (mg/L as CaCO ₃)
Batch	7.89 \pm 0.04	21.5 \pm 0.4	7.87 \pm 0.10	440 \pm 5	100 \pm 2	94 \pm 2
SRF	8.23 \pm 0.05	22.2 \pm 0.4	8.98 \pm 0.09	534 \pm 6	102 \pm 3	96 \pm 3

long \times 0.3 m wide \times 0.3 m deep). Water flow through the channel had a uniform velocity of approximately 12 cm/s. Slurries of either Ni-amended Warden Ditch sediment or Ni-amended clay were added to the head of the SRF channel. Moderate turbidity persisted for the duration of the 48-h tests (Warden Ditch = 32 NTU; montmorillonite = 23 NTU; kaolinite = 38 NTU), although a fine layer of clay/silt was deposited in the channel and inside the exposure chambers. Four exposure chambers housing *D. magna*, in addition to four empty chambers used for chemical sampling, were arranged randomly midway along the channel. Chamber windows were oriented toward the side of the channel. Temperature, pH, dissolved oxygen, conductivity, and turbidity were monitored continuously with a sonde. Temperature and water level in the flume were constant over the course of the experiments. Water was sampled for Ni determination at 0, 12, 24, and 48 h and for DOC analysis at 24 h. Water was withdrawn from each of the four empty chambers through sampling ports on the downstream caps and equal-volume aliquots were composited. Controls for these tests consisted of chambers inside beakers in a controlled water bath.

Sample analysis

Total Ni was measured in water and sediment/clay samples. Nickel in filtered and unfiltered water samples was determined by inductively coupled plasma mass spectrometry (ICPMS) according to U.S. EPA Method 6020A [36]. The amount of Ni adsorbed to particles in batch and SRF tests was calculated as the difference between measured concentrations in filtered and unfiltered water and normalized to the mass of TSS determined from a separate aliquot [36]. Distribution coefficients (K_d , L/kg) were calculated from filtered and particle-associated Ni concentrations. Sediments were analyzed by flame atomic absorption spectrophotometry [37] after microwave digestion with 16 M HNO₃ [38]. All Ni analyses were calibrated with an aqueous standard traceable to the U.S. National Institute of Standards and Technology and calibration curves had coefficients of determination >0.997 . Analytical reproducibility averaged 3.4% relative standard deviation (RSD) for replicate analyses of water ($n = 29$) and 1.6% RSD for replicate digestions of solids ($n = 3$). All Ni analyses were well above our detection limits of approximately 0.1 μ g/L for water and about 0.1 mg/kg for a 0.3-g aliquot of freeze-dried sediment.

The DOC was determined with a total organic carbon analyzer following U.S. EPA Method 9060A [39]. Total organic carbon of the sediment and two clays was measured with an elemental analyzer (Carlo Erba NA1500 C/H/N Analyzer; micro-Dumas combustion assay) at the University of Georgia Institute of Ecology Stable Isotope/Soil Biology Laboratory (Athens, GA, USA).

Particle size distribution of Warden Ditch sediment was assayed with methods of Kettler et al. [40]. Silt was defined as particles $<62 \mu$ m in diameter and clay $<4 \mu$ m.

Statistical analysis

Statistical analyses were performed with SAS[®] 9.1.3. All model assumptions were tested and satisfied by the method that

was ultimately used. Statistical tests and calculations are based on measured Ni concentrations. The Ni LC75 was determined with ToxCalc[™] (Tidepool Scientific Software).

RESULTS

Survival of control organisms for all experiments was 100%. In response to measured Ni concentrations of 210, 350, 750, 1,500, 3,100, and 6,200 μ g/L in Ni-only batch experiments, survival of *D. magna* was 100, 83, 65, 53, 15, and 0%, respectively (Fig. 1). From these results, the Ni LC75 was calculated to be 2,150 μ g/L for *D. magna*.

Survival of *D. magna* was unaffected by humate at exposures less than 18 mg C/L in batch experiments, although exposures of 48 and 80 mg C/L decreased survival by approximately 15 and 55%, respectively, relative to lower humate levels (Fig. 2). The potential mitigating effect of humate on Ni toxicity to *D. magna* was investigated in tests that included this range of humate and aqueous Ni added at the LC75 (2,150 μ g/L). Relative to expected survival based on Ni exposure alone (i.e., 25%), only the 18 mg C/L humate treatment enabled greater survival and the 80 mg C/L exposure reduced it (Fig. 2). Observed *D. magna* survival in the humate + Ni LC75 experiment is largely consistent with that predicted from single-stressor tests with Ni and humate alone (Fig. 2), where predicted survival (%) = (% survival in humate) \times (0.25 survival in Ni at LC75). Enhanced *D. magna* survival in the 18 mg C/L humate treatment suggests that organic ligands may have ameliorated Ni toxicity.

Suspension of Ni-amended sediment and clay had a deleterious effect on *D. magna* survival in batch experiments (Fig. 3). For all three Ni-amended solids, survival of *D. magna* decreased as a function of increasing turbidity in batch tests and were consistent with results from SRF experiments with each solid. Substantial differences in *D. magna* survival existed among types of Ni-contaminated SS, with survival of organisms exposed to montmorillonite being significantly less than those exposed to equal turbidities of either Warden Ditch sediment

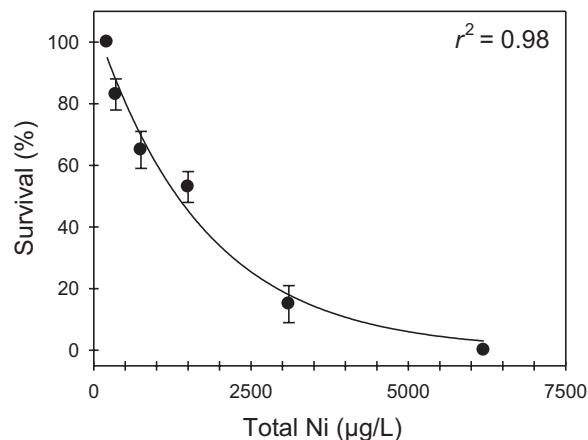


Fig. 1. Survival of *D. magna* versus total aqueous nickel concentration in Ni-only batch experiments. Error bars are one standard deviation of the mean.

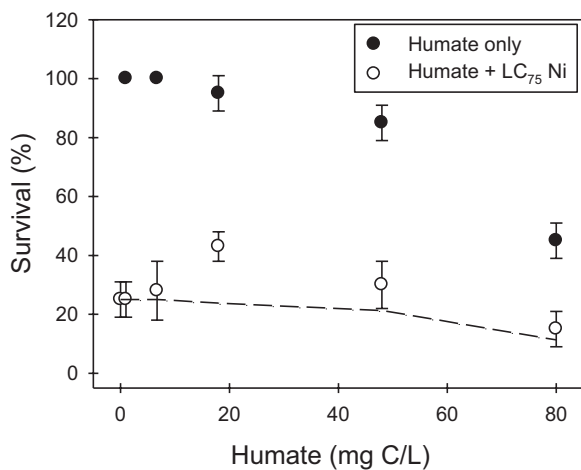


Fig. 2. Survival of *D. magna* exposed to humate only and humate plus aqueous Ni at the LC75 (lethal concentration of Ni for 75% of test organisms = 2,150 µg/L). The dashed line represents the additive predicted survival for humate plus 2,150 µg Ni/L based on combined results from exposures to Ni only and humate only. Error bars are one standard deviation of the mean.

or kaolinite. These results are in marked contrast to batch tests with uncontaminated Warden Ditch sediment, montmorillonite, and kaolinite, which, at 50 NTU, had no effect on survival after 48 h.

Apparent toxicological differences among the three types of Ni-amended SS were related, in part, to variations in mass of SS. While turbidity was a linear function of suspended mass for each particle type, light scattering varied substantially among the three solids with, for example, 50 NTU resulting from either 66 mg/L of Warden Ditch sediment, 249 mg/L of montmorillonite, or 51 mg/L of kaolinite. *Daphnia magna* survival was related inversely to the concentration of Ni-contaminated suspended sediment among all particle types (Fig. 4), and inter-particle toxicological differences, suggested by results in Figure 3, were an artifact of using turbidity as a proxy for SS. In contrast, and as noted above, no mortality was observed in tests with uncontaminated SS (no added Ni).

Nickel desorbed from contaminated SS during the experiments. The concentration of dissolved and particle-associated Ni in solution was a function of the type of suspended solid (Table 2). The affinity of Ni for the SS, measured as

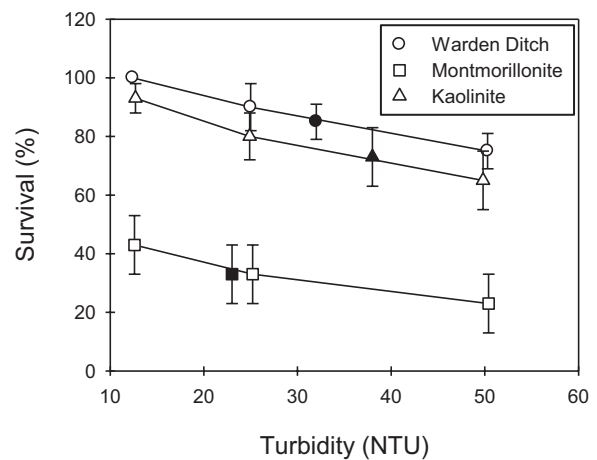


Fig. 3. Survival of *D. magna* exposed to three Ni-contaminated suspended solids in turbid batch experiments (open symbols) and stream-recirculating flume (SRF) tests (closed symbols). Error bars are one standard deviation of the mean. Units for turbidity are nephelometric turbidity units (NTU).

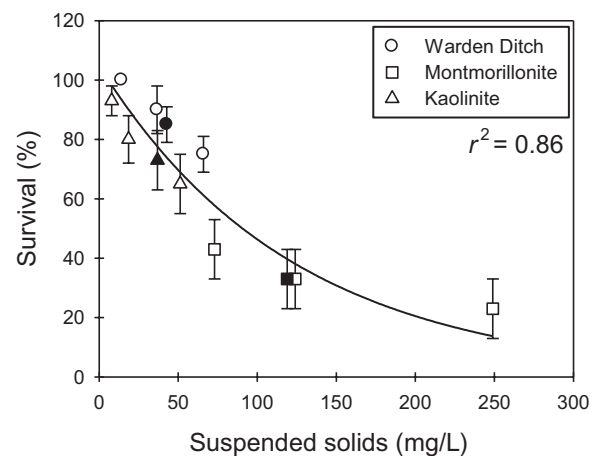


Fig. 4. Survival of *D. magna* versus concentration of Ni-contaminated suspended solids in turbid batch experiments (open symbols) and stream-recirculating flume (SRF) tests (closed symbols). Error bars are one standard deviation of the mean.

Table 2. Mean measured Ni concentrations and calculated distribution coefficients for tests with suspended solids (SS)

Arena	Treatment	Sediment type	Turbidity (NTU ^a)	Suspended sediment (mg/L)	Dissolved Ni (µg/L)	Particle Ni (µg/L)	log <i>K_d</i> (L/kg)
Batch (4-L beakers)	SS + Ni	Warden Ditch	12.4	14	59	18	3.85
			25.0	37	160	60	3.96
			50.3	66	310	150	3.86
		Montmorillonite	12.6	73	195	46	3.51
			25.2	124	270	120	3.56
			50.4	249	640	300	3.28
	Kaolinite	12.7	8	53	0.1	2.39	
		24.9	19	110	1.0	2.72	
		49.8	51	210	4.4	2.62	
		53.5	66	430	170	3.77	
SRF ^b (480-L flume)	SS + Ni	Warden Ditch	53.9	249	1200	160	2.73
		Warden Ditch	32.1	66	330	190	4.13
		Montmorillonite	23.0	249	440	490	3.63
		Kaolinite	38.4	51	380	57	3.61

^aNephelometric turbidity units.

^bStream-recirculating flume.

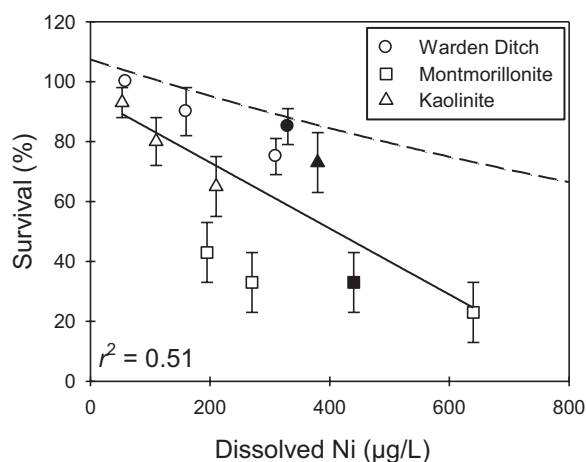


Fig. 5. Survival of *D. magna* related to dissolved (<math><0.2\mu\text{m}</math>) Ni in turbid batch experiments (open symbols) and stream-recirculating flume (SRF) tests (closed symbols). The dashed line is the modeled linear regression curve for survival versus Ni-only exposure from Figure 1. Error bars are one standard deviation of the mean.

the distribution coefficient, was relatively consistent among turbidity treatments for each particle type, with Ni adsorbing more strongly to Warden Ditch sediment ($\log K_d = 3.89 \pm 0.06$) than to either montmorillonite ($\log K_d = 3.45 \pm 0.15$) or kaolinite ($\log K_d = 2.58 \pm 0.17$) in batch tests. Distribution coefficients were comparable, or increased slightly, in stream recirculating flume experiments with the same solids.

Survival of *D. magna* exposed to suspensions of Ni-contaminated sediment and clay was less than exposure to either dissolved Ni or SS alone. Survival of the organisms decreased with increasing dissolved Ni (Fig. 5), resulting from desorption from Ni-amended particles, and rates were substantially less than those for either dissolved Ni only (dashed line in Fig. 5) or suspended particles alone (100%). This suggests that either dissolved Ni and SS acted synergistically to reduce survival of *D. magna* or that test organisms also may have ingested particle-associated Ni.

Humate (7 mg C/L) was added to 50-NTU suspensions of Ni-amended Warden Ditch sediment and montmorillonite in batch experiments to examine a potential ameliorative effect on Ni toxicity. Relative to suspensions without added humate, addition of the ligand increased substantially both the solubility of Ni and survival of *D. magna*. Added humate enhanced dissolved Ni by approximately 40% for Warden Ditch sediment and about 90% for montmorillonite suspensions (Table 2). Further, addition of humate enabled greater survival of *D. magna* exposed to suspensions of Warden Ditch sediment ($93 \pm 10\%$ vs. $75 \pm 6\%$ without humate) and montmorillonite ($50 \pm 8\%$ vs. $23 \pm 10\%$ without humate).

DISCUSSION

This research focused on investigating the effects of two environmentally relevant water-quality parameters—type and concentration of suspended particles and humic material—that can be used to refine present predictive models used to protect ecosystem quality. Specifically, moderate levels of uncontaminated SS did not cause mortality to *D. magna*. Maximum suspended concentrations of Warden Ditch sediment (66 mg/L), montmorillonite (249 mg/L), and kaolinite (51 mg/L) used in our tests are within the range of SS loads determined for 60 major rivers, with most between 20 and 1,000 mg SS/L [41]. Results from our experiments with uncontaminated SS are

consistent with those of Weltens et al. [18], for example, who found exposure of *D. magna* to 500 mg/L suspensions of clay, sand, and peat resulted in no significant mortality.

Exposure of *D. magna* to Ni-contaminated suspended particles resulted in significant mortality that increased with the amount of suspended material and concentration of Ni desorbed from the particles. Given that the maximum levels of SS used in these tests were found to be nontoxic to *D. magna*, these results suggest that either dissolved or dietary Ni, or potentially a combination of the two, was the principal cause of toxicity. The general assumption is that the dissolved fraction of a toxic substance is mainly responsible for toxicity to aquatic organisms [10–16]. However, survival of *D. magna* exposed to suspensions of Ni-contaminated sediment and clay, and associated desorbed Ni, was substantially less than that of organisms exposed to comparable concentrations of dissolved Ni alone (Fig. 5). This suggests that aqueous Ni and SS have a synergistic effect: the interaction of SS and Ni produced a total effect greater than the sum of individual components. Alternatively, enhanced toxicity in the presence of SS, relative to aqueous Ni only, also may be attributed ingestion of particle-associated Ni, although we did not examine dietary versus aqueous exposure in the present study [42].

We observed toxicological differences among equal turbidities of a sediment and two clays that were amended with approximately equal amounts of Ni. However, these interparticle differences were not apparent when TSS, as opposed to NTU, was used as a measure of suspended solids. Variability in the light scattering ability of natural particles, especially in dynamic fluvial systems, argues against the future use of NTU as a proxy for SS.

Dissolved organic carbon reduced Ni toxicity. Complexation by DOM can alter metal bioavailability and toxicity to aquatic organisms when the free metal ion is the main bioavailable species (see review by Campbell [43]). Generally, survival of *D. magna* exposed to Ni-amended Warden Ditch sediment was greater than those exposed to montmorillonite and kaolinite. This may be attributed to either Ni having a relatively greater affinity for Warden Ditch particles (8% organic content) or complexation of dissolved Ni by dissolved organic ligands that partitioned from the natural sediment. The latter hypothesis is supported by the observation that, at a comparable level of total dissolved Ni, nickel appeared to be less toxic to *D. magna* in tests with suspended Warden Ditch sediment. It is also supported by the observation that Ni toxicity was attenuated in tests with added humate, with and without suspended particles, corroborating the research of Arias et al. [44].

In the Ni + humate batch experiments, increasing concentrations of humate resulted in greater survival of *D. magna*, despite the toxic Ni concentration (LC75), yet only up to a threshold. With increasing humate, greater rates of survival would be expected because dissolved organic ligand would, in theory, be available to complex Ni and attenuate toxicity to *D. magna*. Nevertheless, as levels of humate increased, survival of *D. magna* was reduced, which may be attributed to humate clinging to their appendages and inhibiting moving/feeding [42]. Results of the characterization of colloidal humic-bound Ni and uranium in the filtered fraction of contaminated sediment extracts [45] suggested that Ni was potentially bioavailable because the humic-bound Ni was present mainly as labile complexes or the free ion. Thus, a combination of the Ni LC75 and the relatively high humate concentration caused the survival of *D. magna* to decrease rather than increase at higher levels of humate.

The median log K_d of Ni in oxic surface water is 4.6 (range 3.5–5.7, $n = 30$) [21]. Our experimental distribution coefficients agreed reasonably well with this range. Nickel adsorption to clay surfaces was substantially less than that to the Warden Ditch particles, which might be expected given the affinity of Ni for organic ligands [7,8]. In other research, adsorption of the metal by clay minerals increased with increasing pH until the metal ions were precipitated as hydroxide minerals above pH 8.0 [26,46]. Decreased adsorption at low pH is due to competition between metal ions and protons for adsorption sites on the clay surface [10]. The active sites on clay surfaces are weakly acidic; these sites gradually are deprotonated at higher pH resulting in increased adsorption of Cu(II) and Ni(II) [46–49]. Conversely, adsorption decreased with increasing ionic strength [10,46–49].

As expected, the adsorption capacity of montmorillonite was greater than that of kaolinite. Bhattacharyya and Gupta [47,48] observed that montmorillonite had a much greater initial rate of Ni uptake than kaolinite, which might be due to the high specific surface area and CEC of montmorillonite as compared to kaolinite. In general, and due to greater Langmuir monolayer capacity, the adsorption capacity of montmorillonite (and modified forms) was enhanced compared to kaolinite (and modified forms) [46–49].

The physicochemistry of the milieu clearly affects the flux and bioavailability of Ni. Beyond its direct connection with bioavailability, Ni fate is dominated by sediment type, solids level, distribution, and speciation. The concentration of SS influences the toxicity of exchangeable Ni. Therefore, SS should be considered as a separate compartment and key factor in risk assessments. Moreover, inclusion of Warden Ditch sediment in the present study illustrates the differences and complexity of natural systems relative to controlled, clay-only exposures. The addition of humate to the exposure condition further shows ligand availability as a factor affecting metal bioavailability in natural systems [49]. The results of the present study suggest that while dissolved Ni is a good predictor of bioavailability and toxicity, suspended sediment and dissolved organic ligands have important geochemical regulation over partitioning, speciation, and associated toxicity of Ni.

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