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Cover Page Footnote

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EFFECT OF SOIL WASHING ON PETROLEUM-HYDROCARBON DISTRIBUTION ON SAND SURFACES

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ABSTRACT

A soil washing study was performed to evaluate the treatability of New River sand contaminated in the laboratory with a petroleum distillate. Unaltered and base-extracted sands were mixed with petroleum hydrocarbons, equilibrated, and washed with water or a surfactant at two different pH values (7 and 12). The surfactant had no significant effect on contaminant removal efficiencies at neutral pH. Treatment efficiencies of base-extracted sand particles were 10 to 13% higher than for the unaltered sands. Scanning electron microscopy (SEM) with elemental X-ray microprobe was used to determine the distribution of iron and carbon on the New River sand surface. Qualitative interpretations of the SEM/X-ray photomicrographs disclosed that iron oxides were associated with organic carbon on the sand surfaces, with sulfur believed to be a constituent of the petroleum contamination. Low petroleum removal efficiencies for New River sand observed in previous studies were believed to be influenced by the high iron oxide content of the sand and the affinity of these metal oxides to bind natural and petroleum-derived organic carbon.

Key words: soil washing, petroleum hydrocarbons, surfactant, humic acids, SEM

INTRODUCTION

Soil washing and flushing have been proposed as possible remediation technologies for soils contaminated by petroleum hydrocarbons and other hydrophobic organic chemicals (Nash, 1987; Nash and Traver, 1988; Nunno et al., 1988; Esposito et al., 1989; Pheiffer, 1990). The effectiveness of soil washing and flushing processes was recently summarized in a critical review of physical/chemical treatment technologies for organically contaminated soils and sediments (Fox, 1996). The soil washing process separates bulk contaminated soils into several fractions based on particle size. The perception has been that sand-sized and larger soil particles can be treated to acceptable endpoints using water augmented with extracting agents. This often results in up to 60% reduction in the volume of contaminated material to be disposed or treated further by using a more rigorous cleanup process. *In situ* soil flushing applications have also attempted to capitalize on the relatively larger particle size and predominantly mineral character of typical aquifer materials. The larger particles, because of their smaller surface area-to-volume ratio and the absence of significant surface charge, are more readily decontaminated to stipulated cleanup levels during soil washing.

Retention of organic contaminants on coarser soil fractions and aquifer material after soil washing or flushing may be influenced by several factors other than particle surface area, including the hydrophobicity of the contaminant, the properties of the washing medium, and the characteristics of the soil particles. Extremely hydrophobic contaminants such as four- and five-ringed polynuclear aromatic hydrocarbons (PAHs) and high molecular weight alkanes, both constituents of petroleum products, may not readily partition from a soil surface into an aqueous wash fluid. The use of surface-active additives that enhance the mobility of such contaminants in the washing fluid often has

a large impact on the effectiveness of soil washing and flushing (Abdul et al., 1990; Jafvert et al., 1994; Roy et al., 1997; Kommalapati et al., 1997). Similarly, the addition of extraction or chelating agents and pH adjustments can significantly improve contaminant removals (Esposito et al., 1989). The use of such additives, however, results in the production of a more complex spent wash fluid that is difficult to treat or dispose.

Soil organic matter (SOM) content has been implicated as the primary factor governing the interactions between organic contaminants and soil particles (Gschwend and Wu, 1985; Lee et al., 1990; Rutherford et al., 1992; Weber et al., 1992). Slow rates of desorption or mass transfer of contaminants from SOM matrices can render the soil washing process uneconomical for coarser material that may have large amounts of organic carbon. Mineral attributes of the soil or aquifer material, such as the presence of surface metal oxides, may also exert significant control on the extent to which SOM or organic contaminants adhere to the mineral domain of the soil particle (Gu et al., 1994; Evanko and Dzombak, 1998; Kaiser et al., 1998).

In earlier work, where we evaluated the treatability of three soils (Salem, Eagle Point, and New River) using soil washing and biotreatment (Dove et al., 1991, 1992; Bhandari et al., 1994), we found that the sand fraction of the New River soil was resistant to physiochemical and biological treatment. Figure 1 illustrates some results from these earlier studies. Biodegradation of the petroleum hydrocarbon from pre-washed sands was studied in miniature compost reactors. Total petroleum hydrocarbon (TPH) concentration in the New River sand after soil washing (at time = 0 days) was nearly four times greater than that on other sands evaluated. The 90-day biotreatment resulted in final TPH levels of approximately 600 mg/kg for New River sand as compared to 50 mg/kg for Salem and Eagle Point sands.

We hypothesize that the surface chemistry of New River sands, especially the mineral oxide content, may have been responsible for the low TPH removal achieved for these sands. A recent study by Ghosh et al. (2000) utilized mass spectrometric and spectroscopic techniques to study the location of polynuclear aromatic hydrocarbons (PAHs) on sediment particles. Scanning electron microscopy (SEM) techniques can provide detailed three-dimensional views of mineral and organic surfaces with a depth of focus that is of the order of tens of microns. In the study described here, we utilized SEM in a qualitative mode to study the distribution of iron oxide, soil organic carbon, and petroleum-hydrocarbon constituents on New River sand. Water and surfactant extractions were also performed to probe the factors affecting TPH binding on New River sand.

EXPERIMENTAL APPROACH

Uncontaminated soil used in this study was obtained from the banks of the New River near Blacksburg, Va. The bulk soil was processed as described in Figure 2. Soil fractionation, using a commercial hydraulic screen, showed that the New River soil consisted of approximately 34%

sand, 39% silt, and 27% clay-sized particles. For the purpose of this study, the New River sand fraction was divided into two parts. While one part was washed with distilled water, the other was extracted with 0.1 N NaOH solution ($\text{pH} > 13$) under a nitrogen atmosphere to remove humic and fulvic acids (HA). To allow direct determination of TPH removal efficiencies, the two sands were contaminated in the laboratory with a petroleum distillate as described in detail by Bhandari et al. (1994). Briefly, a volume of distillate obtained from a fuel depot in San Francisco, Calif., was mixed with 50 g sand in a glass bottle to obtain a TPH concentration of approximately 20,000 mg/kg. The initial TPH concentration, however, was found to be inconsistent because of the variability in transferring an exact amount of distillate into the glass bottle. The contents of the bottle were mixed in a mechanical tumbler for four hours and then allowed to equilibrate at 4°C for 14 days.

TPH was quantified according to the procedure outlined by Bhandari et al. (1994). Briefly, 1.0 g soil was extracted using 20 mL of dichloromethane for 12 hours in a 40-mL glass extraction vial sealed with a Teflon-lined silicone septum and a phenolic cap. Dichlorobenzene was added as the internal standard. External standards were prepared from a mixture of fuel oil, diesel, kerosene, petroleum distillate, and crude oil dissolved in dichloromethane. Analysis was performed on a Hewlett Packard 5890 gas chromatograph with a flame-ionization detector using a DB-1, fused-silica capillary column.

The contaminated New River sands (base extracted and unextracted) were washed with water or, Citrikleen[®], a commercial nonionic surfactant, at two pHs (pH 7 and 12). Two grams of contaminated sand particles were transferred into 40-mL glass extraction vials containing 35 mL water or surfactant. Triplicate sets of such vials were mixed for 18 hours at $25 \pm 1^\circ\text{C}$. For the pH 12 solution, the wash solution was first purged with nitrogen gas. The headspace in the extraction vials was also replaced with nitrogen to prevent auto-oxidation of the organic matter at high pH.

SEM with elemental X-ray probe was utilized to determine the location and relative concentration of carbon, iron oxides, and sulfur on the sand particles. In this method, the X-rays produced from an SEM electron beam striking the sample are collected and analyzed to determine the elemental composition of the sample. We used SEM to scan surfaces of a population of the sand grains and identify those that had regions of high carbon content. Three sand grains meeting this criterion were selected from each treatment and further examined for the elemental distribution (C, Fe, and S) on their surfaces. This analytical ability afforded a window into the interaction of surface mineral oxides with soil organic carbon and organic carbon-based contaminants.

RESULTS AND DISCUSSION

Washing studies

TPH and total carbon removal efficiencies for the New River sand particles with and without HA are presented in Table I. The average contamination on sand particles with HA intact was

approximately 16,060 ppm or 16.06 mg TPH per gram of soil. Washing the sand with distilled water at pH 7 resulted in 65% removal of TPH. No significant improvement in TPH removal was observed when the nonionic surfactant solution was used at neutral pH (pH 7). Raising the pH of the distilled water to 12 resulted only in a minor increase in TPH removal efficiency (69%). However, a significant enhancement in TPH removal efficiency was evident (from 66% to 73%) when the pH of the nonionic surfactant solution was adjusted to 12.

The initial concentration of total carbon on the sand surface, as determined from the SEM/X-ray signal, was 190 mg/g. Quantification of total carbon by this method included carbon associated with the natural organic matter and petroleum hydrocarbons. Washing the sand with distilled water at pH 7 resulted in 43% removal of total carbon from the sand particles. No major changes in carbon removal efficiencies were observed for water at pH 12 or for the surfactant solution at pH 7. However, removal of total soil carbon was significantly larger (53%) with the surfactant solution at pH 12.

Raising the solution pH can result in swelling or expansion of the soil organic matter structure from a "tight" condensed configuration to a "loose" amorphous one (Schwarzenbach et al., 1993). Data in Table I suggest that a pH-mediated expansion of the SOM structure may have resulted in greater accessibility of the nonionic surfactant to the internal surfaces of the SOM macromolecule. The surfactant was therefore able to reduce the surface tension in the immediate vicinity of the adsorbed petroleum-hydrocarbon molecules and enhance partitioning from the solid phase into the aqueous phase. This appears to have resulted in the higher TPH removal efficiency exhibited when the sands were washed with the nonionic surfactant at pH 12. The data also suggest that accessibility of the surfactant to the sorbate was restricted at neutral pHs, most likely due to the condensed SOM configuration. No enhancement in TPH removal efficiency was observed when the sand was washed with distilled water at pH 12. This result indicates that the action of a surface-active agent was necessary to remove the hydrocarbons, even when raising the pH expanded the SOM structure. The data show no conclusive evidence that raising the pH of the wash solution to 12 resulted in the extraction of humic material from the sand particles.

Sand particles from which humic acids had been removed prior to contamination contained higher initial TPH. Initial petroleum-hydrocarbon concentration on these sands was higher because of inconsistency in the contamination procedure as explained in the experimental section. Significantly higher TPH removal efficiencies were observed for the HA-extracted sand particles at neutral pH. Removal of HA, however, had no major impact on total carbon removal efficiencies. Although initial contamination on the HA-extracted sands was greater, these sand particles were more readily cleaned with TPH removal efficiencies 10 to 13% larger than sand particles with HA intact. Note that the base extraction procedure removes only humic (and fulvic) acids from sand particles, leaving behind the alkali-insoluble organic matter on the sand (Schnitzer, 1991). The HA-extracted

sand was not devoid of organic material, but contained organic matter whose composition had been altered by the selective extraction of humic acids. The improvement in removal of TPH from the HA-extracted sand particles alludes to the role played by these organic macromolecules in the retention of hydrophobic organic chemicals on particle surfaces.

Results from the washing study appear to suggest that humic acids can exert a significant influence on the treatability of petroleum-hydrocarbon contaminated sands. TPH removal efficiencies for HA-extracted sands were considerably higher despite the higher initial contamination levels. Desorption of contaminants occurred more readily from the base-extracted sand as compared to the sand with HA intact. As in the case of the sand with HA intact, the surfactant had no significant effect on TPH removal for the base-extracted sands at neutral pH.

SEM studies

Our earlier studies had suggested that soils of similar particle-size distribution but of different origins manifested different TPH-retention characteristics (Bhandari et al., 1994; Dove and Novak, 1992). To obtain a qualitative understanding of this observation, we conducted SEM/X-ray microprobe studies and interpreted the resulting SEM photomicrographs. These photomicrographs are presented in Figures 3 and 4.

Figure 3a shows a magnified view of a 0.2 mm x 0.2 mm surface area of a contaminated New River sand particle (unextracted) washed for 18 hours with water at neutral pH. As is clear from the picture, the sand surface is not smooth but consists of irregularities such as ridges, troughs, and cavities. These surface irregularities appear to provide sites on the edges of mineral lattices capable of retaining high concentrations of contaminant. Figure 3b is a SEM photomicrograph that shows regions of high iron concentration. These regions appear to correlate strongly with the ridges seen on the sand particles. Figure 3c is a photomicrograph showing the distribution of carbon on the sand particle. This carbon includes the petroleum-hydrocarbon contaminant and the natural organic matter associated with the sand particle. It should be noted that the carbon distribution is strongly related to the distribution of iron on the sand surface. Large concentrations of carbon also appear to be associated with the ridges and troughs on the sand surface at the upper and lower right-hand corners in view (Figure 3c).

To confirm the relationship between high iron and high carbon regions on New River sand, a more detailed analysis was done for the high carbon region on the top right-hand corner of the sand particle shown in Figure 3. These SEM photomicrographs are presented in Figure 4. In these pictures, the target area in Figure 3 is rotated by about 120° in the clockwise direction. Figures 4a and 4b show the distributions of carbon and iron, respectively. As can be seen in Figure 4b, the presence of carbon on top of the iron appears to prevent the X-ray elemental probe from readily detecting the underlying iron. The figure also shows that the carbon on the sand surface preferentially associates with regions of high iron content. Several researchers have observed strong binding

and high hysteresis coefficients for natural organic matter (NOM) and NOM-analogue organic acids adsorbed to iron-oxide surfaces (Gu et al., 1994; Evanko and Dzombak, 1998). These researchers attributed the strong association between the organic matter and iron oxides to ligand exchange between carboxyl, hydroxyl, and phenolic functional groups in natural organic matter (NOM) and iron oxide surfaces. Kaiser et al. (1998) found that colloidal NOM mobilized from forest soils was retained on mineral soils mainly due to its strong association with Fe and Al hydrous oxides.

The distribution of petroleum hydrocarbon on the sand surface was determined by scanning the surface of the sand for sulfur. Although soil organic matter may contain 0.3 to 1% sulfur (Schnitzer, 1991), the sulfur concentration in petroleum is usually up to an order of magnitude greater (Orr and Damste, 1990). Figure 4c illustrates the distribution of elemental sulfur on the New River sand surface. Although sulfur concentration on the sand surface is low, its distribution conforms well with that of the carbon and iron, indicating that petroleum hydrocarbons may have contributed to the carbon signal shown in the photomicrographs.

Figures 5a and 5b show similar photomicrographs of the distribution of iron and carbon on a different grain of New River sand. The relationship between the distribution of iron and carbon on the sand grain appears to give strength to our contention that the location of organic matter is related to the presence of iron oxides on sand surfaces. Surface metal oxides can play a significant role in binding petroleum-hydrocarbon contaminants directly or by creating high organic matter regions into which petroleum contaminants may partition.

SUMMARY AND CONCLUSIONS

This investigation was conducted to determine the reasons for high petroleum-hydrocarbon retention observed for New River sand during past soil washing and biotreatment studies (Bhandari et al., 1994). New River sand had exhibited residual hydrocarbon levels that were approximately four times higher than other sands evaluated in those studies. In the experiments described in this manuscript, we first contaminated and then washed the New River sand. Results suggest that the organic matter clearly played a role in the extent and intensity of hydrocarbon association. Removal of humic acids significantly improved TPH removal efficiencies from the sand particles. Use of a nonionic surfactant improved TPH removal at a pH of 12.

Analysis of SEM/X-ray microprobe photomicrographs illustrated the relationship between iron and carbon distribution on the sand surfaces. The New River soil was a young alluvial soil with sand grains richer in iron oxides, compared to the other two soils that were evaluated by Bhandari et al. (1994). The high-energy binding of SOM or TPH to surface iron oxides or hydroxides was possibly responsible for their preferential association with regions of high iron content on the sand grains. Organic matter associated with iron-rich regions on sand surfaces is also likely to act as a preferred domain for further TPH adsorption. The distribution of sulfur in this study was indicative

of a carbon signal that consisted, at least in part, of the petroleum hydrocarbon added to the soil. It is clear that the tendency of the New River sand to resist physicochemical or biological treatment to the levels achieved with other sands (Bhandari et al., 1994) was primarily due to the strong associations between the iron, SOM, and the TPH contaminant. In practical situations, therefore, it may be necessary to evaluate soil-particle characteristics in greater detail before selecting a treatment method. Strong associations between mineral surfaces, SOM, and organic contaminants may severely limit the success of both conventional physicochemical and biological processes.

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Table 1. Total carbon and total petroleum hydrocarbon (TPH) removal efficiencies from New River^a sand.

TREATMENT	TPH ^b	Total Carbon ^c	Removal Efficiency (%)	
	(mg/g)	(mg/g)	TPH	Total Carbon
HA Intact				
Initial	16.06 ^d (1.3) ^e	190 ^f (2.4) ^e		
H ₂ O, pH 7	5.67 (0.09)	109 (1.5)	65	43
Surfactant, pH 7	5.46 (0.05)	114 (2.3)	66	40
HA Removed				
Initial	23.31 (2.2)	183 (0.5)		
H ₂ O, pH 7	5.13 (0.08)	102 (0.3)	78	44
Surfactant, pH 7	5.56 (0.08)	98 (2.3)	76	46

^a total iron content of New River sand particles = 7500 mg/kg (5000 mg/kg amorphous, 2500 mg/kg crystalline)

^b as determined by DCM extraction/GC-FID analysis

^c as determined from SEM signal

^d mean of three samples

^e standard deviation

^f mean of three grains scanned

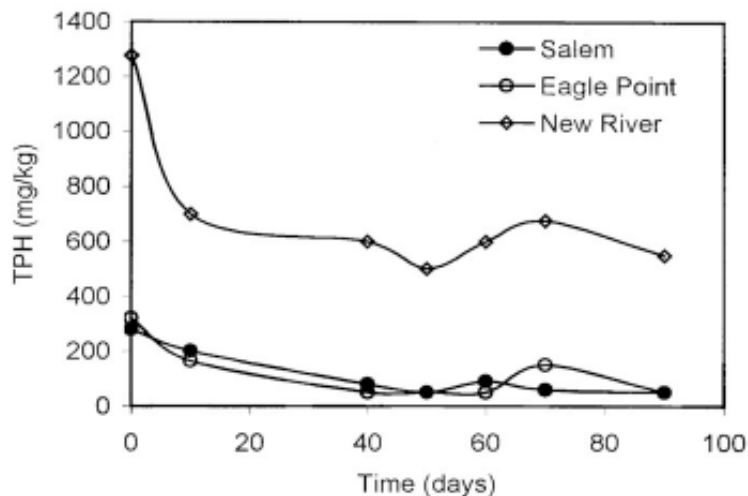


Figure 1. Biodegradation of petroleum hydrocarbon from washed Salem, Eagle Point, and New River sands in miniature compost reactors (adapted from Bhandari et al., 1994).

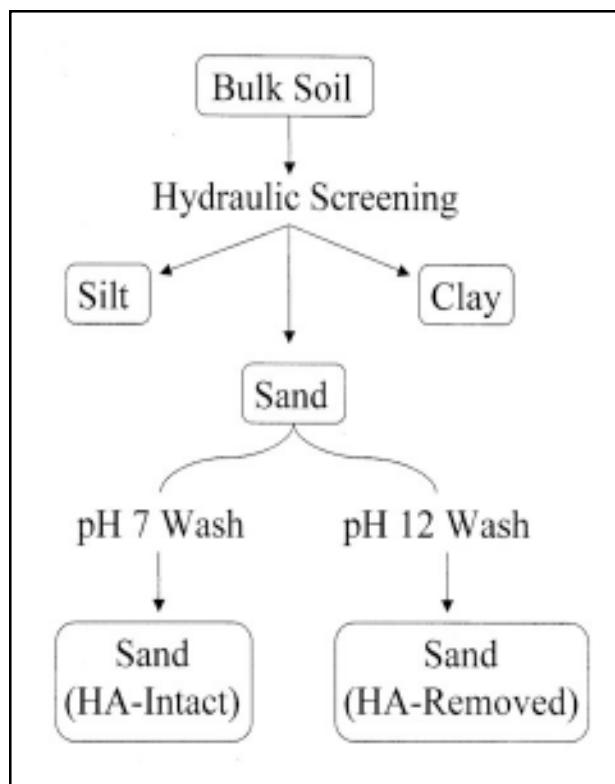
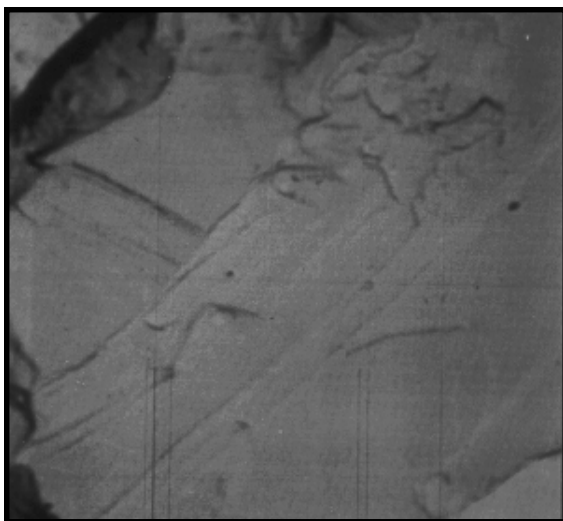
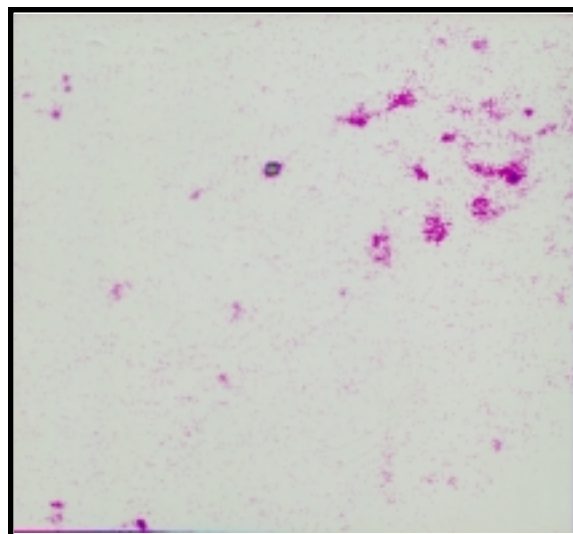


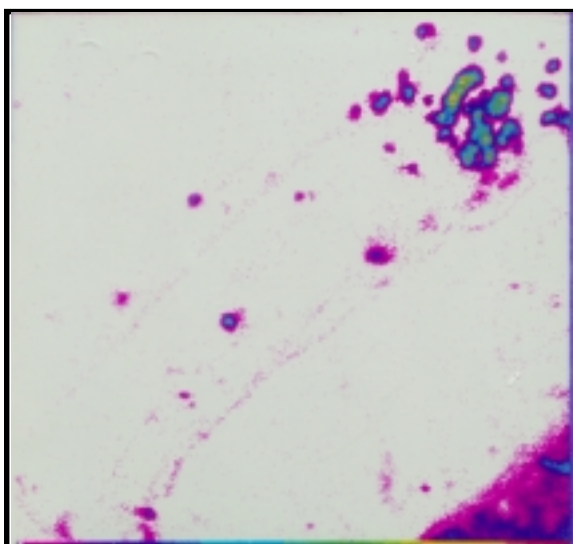
Figure 2. Flow chart illustrating the sample preparation process for New River sands. HA = humic acid.



(a) Sand Surface

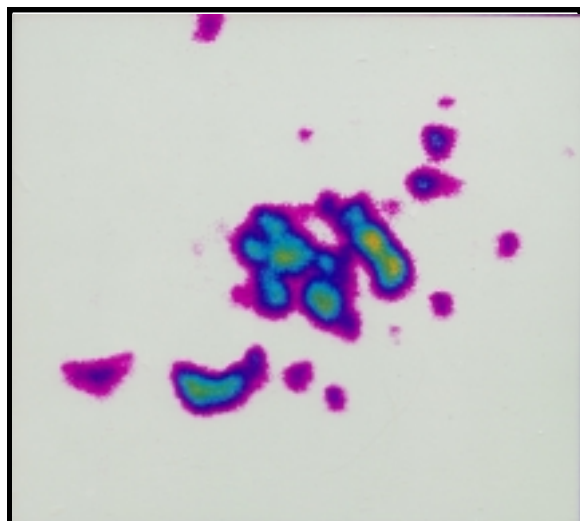


(b) Iron

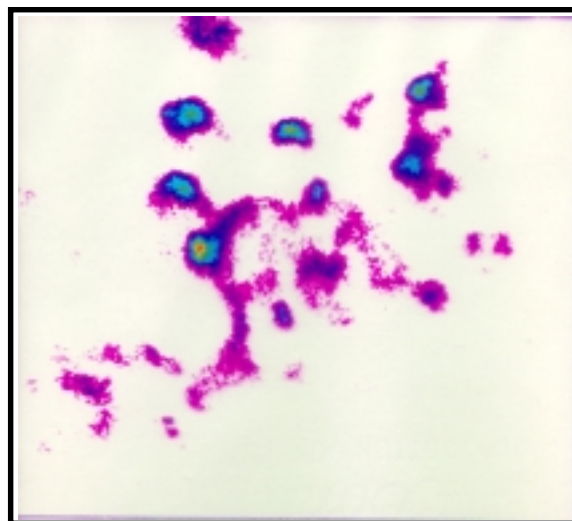


(c) Carbon

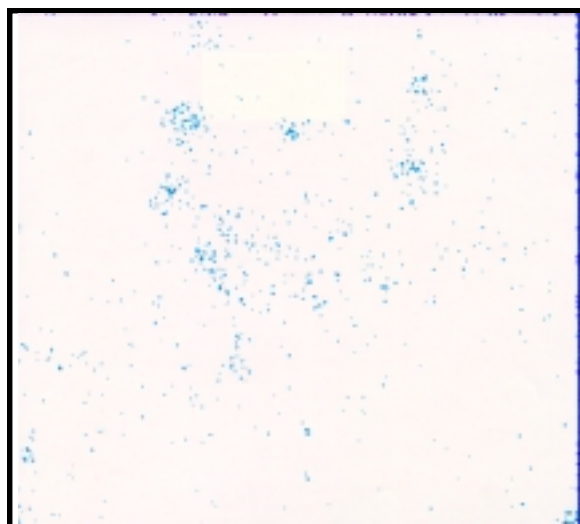
Figure 3. Photomicrographs of SEM/X-ray elemental microprobe analysis of New River sand particle. View = 0.2 mm x 0.2 mm.



(a) Carbon



(b) Iron



(c) Sulfur

Figure 4. Photomicrographs of SEM/X-ray elemental microprobe analysis of New River sand particle. Close-up view of the top right-hand corner of Figure one, rotated 120° in clockwise direction.

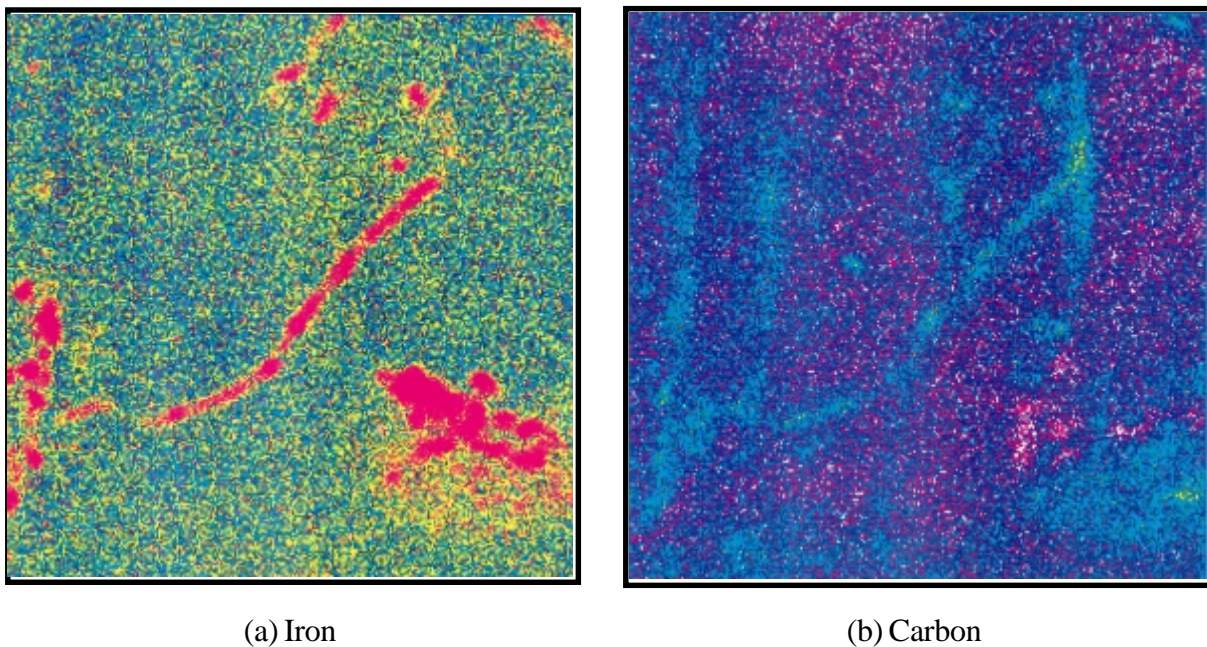


Figure 5. Iron and carbon distribution on New River sand particle as determined by SEM/X-ray microprobe analysis. Note that regions of high carbon shown in blue in (b) correspond closely to regions of high iron shown in red in (a).