BIOSOLIDS USE FOR RECLAIMING FLUVIAL MINE TAILINGS

C.L. Freeman[1], J.A. Ippolito[2], M.E. Stromberger[1], K.A. Barbarick[1], and E.F. Redente[3,4]

[1]Department of Soil and Crop Sciences
C-127 Plant Sciences Building
Colorado State University
Fort Collins, CO 80523-1170

[2]USDA-ARS Northwest Irrigation and Soils Research Laboratory
3793 N. 3600 E.
Kimberly, ID 83341

[3]Department of Forest, Rangeland and Watershed Stewardship
Colorado State University
Fort Collins, CO 80523-1472

[4]MWH Americas, Inc.
1825 Sharp Point Drive, Suite 118
Fort Collins, CO 80525

ABSTRACT

This study was conducted to determine the effect of biosolids and lime on reclamation of a heavily contaminated metal site. Within the Superfund area near Leadville, CO, biosolids and lime were amended (1998) to a 1 ha site at rates of 240 Mg ha^{-1} each. In 2006, soil samples were collected on a 10 m x 10 m grid to a depth of 30 cm across the site. Basic soil analysis included pH, EC, total C and N, inorganic and organic C, and NO_3-N and NH_4-N. A sequential fractionation for metal contaminants of concern (Cd, Cr, Fe, Pb, Mn, and Zn) identified associations with: 1) soluble/exchangeable; 2) specifically sorbed/weakly bound; 3) non-crystalline Fe/Mn oxides; 4) crystalline Fe/Mn oxides and organically complexed; 5) residual organic; and 6) residual inorganic phases. Sequential extraction data was cross correlated with basic soil analysis. Basic soil analysis were affected by both lime and biosolids applications. Cadmium was found primarily in mobile phases, Cu, Fe, Pb, and Mn in more resistant phases, and Zn distributed equally among all soil fractions. Metals were negatively correlated with basic soil analysis. The greatest mobile-phase metal concentrations were observed at the site's south end. This may have been due to a lack of uniformly applied or incorporated biosolids, or not enough lime applied to raise soil pH and complex metals in more immobile phases. If mobile phases were present over the entire site prior to reclamation, then a positive phase shift has occurred towards more immobile metal phases following reclamation.

INTRODUCTION

The Rocky Mountains in Colorado have a mining legacy ranging from gold to uranium. Several mines are still in operation today, yet most mines have been shut down or abandoned. The Colorado gold rush began in 1859 and during its history produced 45 million ounces of gold (Colorado Geological Survey, 2005). Silver was accidentally discovered in Leadville, CO while panning for gold. When recognized as silver ore, this find opened the prospect for other minerals to be mined in Leadville, including zinc and lead.

As a consequence of wide spread mining and smelting prior to regulation, extensive contamination has occurred in this region. A major area of contamination drains from California Gulch just east of Leadville, CO. Great quantities of wastes were released into this tributary in the form of metal sulfides, resulting in reaction between sulfides and the atmosphere, producing sulfuric acid. The primary source of this acid mine drainage originates from the Yak Tunnel, which is connected to 17 mines (U.S. Environmental Protection Agency, 2007a) just east of Leadville. Aside from acid drainage, the water contains elevated concentrations of dissolved metals such as iron, lead, zinc, manganese, and cadmium (U.S. Environmental Protection Agency, 2007a). The entire affected area spans 43 ha^2 (U.S. Environmental Protection Agency, 2007b) and includes Leadville, CO. This area was placed on the National Priorities List (NPL) of Superfund sites (the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)) in September 1983 and cleanup continues to this day. In 1994, the EPA divided the site into 11 geographically-based areas called operable units (U.S. Environmental Protection Agency Region 8, 2005). The Arkansas flood plain, or operable unit 11, has been included in the Superfund project because of fluvial tailings deposits that are found along the river.

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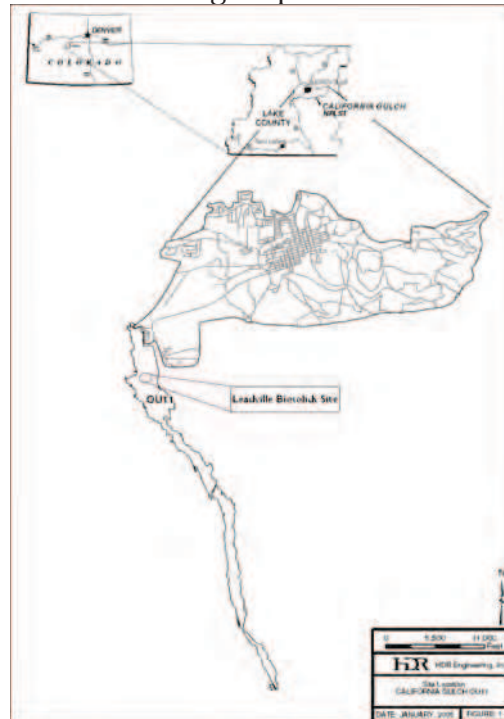
In an initial site assessment, Levy et al. (1992) found excessive total soil concentrations of copper, cadmium, iron, lead, manganese, and zinc within operable unit 11. Total metal concentrations ranged from 14 to 1200 mg Cu kg^{-1}, 3 to 110 mg Cd kg^{-1}, 16500 to 45200 mg Fe kg^{-1}, 46 to 49000 mg Pb kg^{-1}, 1740 to 8760 mg Mn kg^{-1}, and 44 to 12100 mg Zn kg^{-1}. Soil metal fractionation determined water extractable, exchangeable, organically bound, and oxide-bound. Cadmium, Pb, and Zn were all primarily found in the oxide fraction, while Cu was predominantly associated with the organic fraction (Levy et al., 1992). Metal transport, and subsequent environmental contamination within this system, occurred primarily as alluvial deposition.

Damaging mining effects on soil, either from direct mining deposits or indirect alluvial or aeolian deposition, have been observed over decades and centuries. Acidic mine drainage can decrease soil pH, solubilize metal contaminants, and potentially increase forage metal uptake. Soil factors that contribute the greatest extent in terms of metal bioavailability are pH, organic matter, clay content, surface charge density, soil solution composition, redox potential, rhizosphere interactions (Naidu et al., 2003), competition among metals, carbonates, chloride ions, and accumulation in plants (Adriano, 2001). Metal ions transported within mine drainage can rapidly interact with soil mineral and organic phases to form quasi-equilibrium with soil solution metal ions (Naidu et al., 2003), thus controlling metal solubility.

Among factors that influence metal availability, pH is the most widely utilized to improve the understanding of metal availability. Soil pH can be viewed as the master driver of all the other factors because it can affect the surface charge of layer silicate clays, OM, and oxides of Fe and Al (Adriano, 2001). It also influences precipitation-dissolution reactions, redox reactions, mobility and leaching, dispersion of colloids, and the eventual bioavailability of the metal ions (Adriano, 2001). As pH increases, a decrease in the mobility of cationic trace elements occurs, due primarily to the aforementioned soil reactions. Adriano et al. (2004) stated that the effect of pH values >6 in lowering free metal ion activities in soils can be attributed to the increase in pH-dependent surface charge on Fe, Al, and Mn oxides, chelation by organic matter, or precipitation of metal hydroxides. Metals can form both inorganic and organic complexes. With an increase in pH, the carboxyl, phenolic, alcoholic, and carbonyl functional groups in soil organic matter dissociate, thus increasing the affinity of ligand ions for metal cations (Adriano et al., 2004). Immobilization of metals predominantly occurs during precipitation in alkaline soils and in the presence of anions, especially when metal ion concentrations are high (Adriano, 2001).

Soil is one of the most important natural resources, and thus remediating mine land sites for ecosystem sustainability is essential. The soils natural "cleaning" action is primarily controlled by metal physico-chemical reactions with soil components carrying surface charge, and by soil microbial biochemical transformations (Bolan et al., 1999; Adriano, 2001; Bolan and Duraisamy, 2003). Remediation can be performed *ex-situ* or *in-situ*. *Ex-situ* remediation is carried out by contaminated soil extraction/removal with subsequent on- or off-site treatment.
Ex-situ treatment options consist of land treatment, thermal treatment, asphalt incorporation, solidification/stabilization, chemical extraction, and excavation (Sparks, 2003). *In-situ* remediation occurs on-site to stabilize contaminants, can be considered a more natural clean-up process, and in most cases is significantly less expensive than *ex-situ* remediation options. *In-situ* treatment options include volatilization, biodegradation, phytoremediation, leaching, vitrification, isolation, and passive remediation (Sparks, 2003).

Most *in-situ* techniques require amendments to help promote contaminant degradation/stabilization. Typical amendments, applied alone or in combination, include lime, manure, and fertilizers (nitrogen, phosphate, etc). Amendments accelerate natural processes such as metal sorption, precipitation, and other complexation reactions to reduce trace element mobility and bioavailability (Bolan and Duraisamy, 2003; Hartley et al., 2004; Pérez de Mora et al., 2005). Amendments can also enhance microbial activity, colonization and development of plant communities, essentially restarting soil nutrient cycling (Madejon et al., 2006).

Recently, biosolids or composted biosolids have become a more frequently used amendment complimenting the *in-situ* remediation process. Lime, in conjunction with biosolids, has been used to reduce the total acidity of acidic mine spoils and thus raise the pH at which the soil is buffered. Due to this pH increase, liming will increase the negative charge on oxides, clays, and organic matter effectively reducing the mobility of trace elements (Adriano, 2001). When limestone is used, supplied carbonate consumes excess protons from soil solution and exchange sites, thus raising pH. Essington (2004) also noted that protons consumed in the initial dissolution of $CaCO_3$ can be released during precipitation of exchangeable Al as gibbsite, and thus there is no net consumption of H^+. The initial buffering effect could be attributed to other metal contaminants when individual metal pH thresholds are met and solid phase precipitation begins.

Pérez de Mora et al. (2005) found composted biosolids application, at a rate of 100 Mg ha^{-1} on a fresh basis at 20-25% moisture content, to a heavy metal contaminated site was effective in significantly reducing metal solubility. This decrease in metal solubility was potentially the result of the organic amendment increasing soil organic matter content, enhancing soil fertility, structure, and water retention (Madejon et al., 2006). Composted biosolids was also effective in buffering soil pH (Pérez de Mora et al., 2005; Madejon et al., 2006), with buffering capacity controlled by non-humic and humic substance functional groups.

The Upper Arkansas River near Leadville, Colorado has been heavily affected by historic mining operations. Mine wastes were generally stockpiled or dumped directly into the river, resulting in fluvial mine tailings depositions along a 22-km stretch (Brown et al., 2005). These deposits are now considered for cleanup under the USEPA CERCLA National Priorities List. In 1998, Brown et al. (2005) incorporated municipal biosolids and agricultural limestone into the surface of alluvial mine tailings found within the Leadville, Colorado CERCLA area to restore ecosystem function. The research site provided an opportunity to study the long-term amendment effects on soil reclamation of fluvial mine tailings. The objective of this study was to identify and relate soil and plant spatial variability across the Leadville, CO site to reclamation success.

MATERIALS AND METHODS

The experimental site was located on the Smith ranch south of Leadville, Colorado, associated along the Arkansas flood plain in the California Gulch Superfund Site. In the summer of 1998, biosolids and lime were both applied at rates of 224 Mg ha^{-1} on a dry weight basis. Materials were mixed on a volume basis using a front-end loader before application (Brown et al., 2005). The amendments were surface-applied using a rear throw spreader with floatation tires and incorporated with a ripper to a depth of approximately 20 cm (Brown et al., 2005). Biosolids and lime were supplied from the Denver Metro Wastewater Facility and Calco Limestone Products (Salida, CO), respectively. The biosolids were anaerobically digested with a solids content of approximately 17% and met Class B criteria for pathogen reduction (Brown et al., 2005; USEPA, 1993).

During the fall of 2006 the site was grid-soil-sampled using 10 m x 10 m sampling coordinates (Fig. 1). South, West, and North sampling boundaries roughly followed the Arkansas River; the East boundary followed a North-South fence-line. Soils were collected to a depth of 30 cm at each grid point; a total of eighty eight soil cores were obtained. The two prominent soils on site were the Rosane loam 1-5% slopes and Newfork gravelly sandy loam, 1-3% slopes (USDA NRCS, 2007). All samples were placed in a cooler and transported to Colorado State University for analysis.
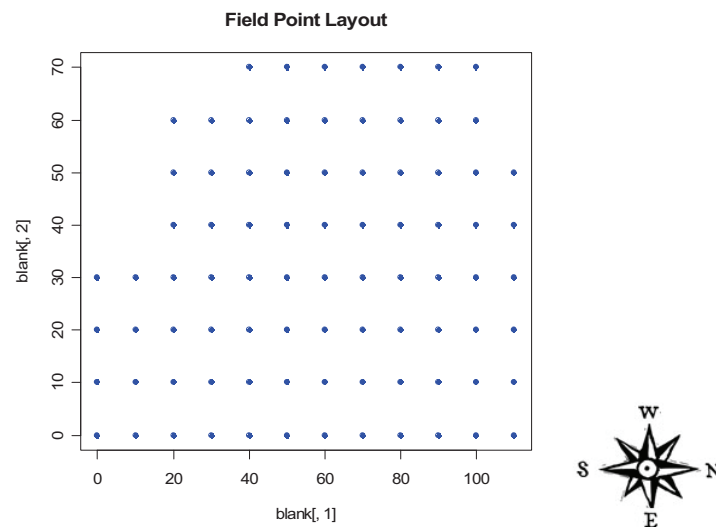

Figure 1. Field Grid-Point Sampling Lay-out.

Soil samples were immediately air-dried and ground to pass a 2mm sieve. Basic soil analysis consisted of pH and electrical conductivity (EC) measured using a saturated paste extract, total C and N determined using a LECO-1000 CHN auto-analyzer, inorganic C measured using a modified pressure-calcimeter method, NO_3-N and NH_4-N concentrations on 2 M KCl extracts, and organic C and N determined by subtracting inorganic C and N content from total C and N concentrations.

Most studies pertaining to soil heavy metal contamination focus on plant-available or total extractable metals. However, these studies are lacking a fundamental understanding of the

potential transformations and ultimate fate of metals in the soil environment. To assess metal fate following reclamation, a six-step metal fractionation separated soils as follows: 1) soluble and exchangeable; 2) specifically sorbed and weakly bound; 3) non-crystalline Fe and Mn oxides (i.e. amorphous phases); 4) crystalline Fe/Mn oxides; 5) residual organic; and 6) residual inorganic (Sloan et al., 1997). The extraction scheme essentially utilizes increasingly harsher extractants to differentiate metal pools. Following each extraction step, all samples were centrifuged, the supernatant filtered through a 0.45µm membrane, and then analyzed using inductively coupled plasma-atomic emission spectroscopy.

Data were statistically analyzed using R version 2.5.0 (The R Foundation for Statistical Computing, 2007). Spatial autocorrelation and cross correlation statistics were used to characterize the site. Moran's I was employed for spatial autocorrelation, which provides a P-Value and a Moran's I number for both normal and randomization assumptions. Randomization was utilized since the data was assumed to not be normally distributed due to grid sampling. To be significantly spatially correlated we considered the two-sided p-value to be ≤0.1, while Moran's I identified either a positive or negative correlation with distance from sampling location. Contour maps were created using datasets that were significantly correlated, to show an overall trend surface across the site. Contour maps underestimate variability do to interpolation of the original data values. Bimoran's I was used for spatial cross correlation statistics between soil metals and basic soil characteristics, which provides a P-Value and a Moran's I number under the randomization assumption only. To be significantly spatially correlated we considered the two-sided p-value to be ≤0.1, while Moran's I identified either a positive or negative correlation with distance from sampling location.

RESULTS AND DISCUSSIONS

Spatial Autocorrelation
  Basic Soil Characteristics
The pH contour map (Fig 2 (a)) illustrated the greatest pH through the middle of the site with lowest concentrations on the south. This could be a function of lime application. Electrical conductivity and inorganic nitrogen contour maps (Fig 2 (b) and (c)) showed greater conductivity and concentration on the north/east side of the site. This could also be a function of the lime application. Organic nitrogen and organic carbon contour maps (Fig 2 (d) and (f)) were variable across the site, potentially a function of biosolids application.

  Cadmium
All six sequential extraction steps for cadmium had two-sided p-values of <0.10. Soluble and exchangeable, specifically sorbed/weakly bound, non-crystalline Fe/Mn oxides, crystalline Fe/Mn oxides & organically complexed, and residual organic all contained greater Cd concentrations on the site's southern portion (Fig 3 (a), (b), (c), (d), and (e)). Residual inorganic Cd (Fig 3 (f)) was opposite, with the greatest concentrations in north side soils. Overall, the greatest Cd concentrations were found in steps 1 and 2, or the soluble/exchangeable and specifically sorbed/weakly bound phases, phases which are plant available and potentially mobile in the soil. If these two relatively mobile phases were present in greater concentrations over the entire site prior to reclamation, then a positive phase shift has occurred towards more immobile Cd phases. Li et al. (2001) noted an increase in Cd sorption with increasing biosolids application, and upon removal of the soil organic phase, Cd sorption persisted. The authors

attributed adsorption to the inorganic fraction provided by biosolids. Hettiarachchi et al. (2003) further showed reduced soil Cd adsorption by removing both the organic C and Fe/Mn fractions. Thus, the addition of biosolids containing appreciable quantities of Fe and Mn oxides could promote Cd sorption in a relatively immobile phase. Ippolito et al. (2007) noted biosolids applied at a site in Colorado contained elevated Fe concentrations due to waste stream $Fe_2(SO_4)_3$ addition for reducing digester H_2S production. Overall, the greater concentrations of mobile Cd phases observed at the south end of the site may have been due to a lack of uniformly applied or incorporated biosolids, or not enough biosolids/lime applied to raise soil pH and complex excess Cd in Fe/Mn oxide phases.

Copper

All six steps for copper had two-sided p-values of <0.10.   Soluble/exchangeable Cu concentration was greater on the site's south/west side (Fig 4 (a)). Specifically sorbed/weakly bound, non-crystalline Fe/Mn oxides, and crystalline Fe/Mn oxides/organically complexed Cu concentrations were greatest on the south and north sides (Fig (b), (c), and (d)). Residual organic and inorganic Cu concentrations were greater on the north side (Fig (e) and (f)). Greatest Cu concentrations were observed in the organically complexed and residual organic forms, a potential function of biosolids application. Adriano (1986) stated that applied or deposited Cu will persist in soil because it is strongly complexed or sorbed by OM, oxides of Fe/Mn, and clay minerals. Relative to phases dominating Cu complexation, Fe/Mn oxides and OM are the most important Cu complexing soil constituents (Jenne, 1977; McLaren et al., 1981). The bulk of the bioavailable soil Cu resides in the organically bound fraction (McLaren and Crawford, 1973). Behel et al. (1983) found that up to 80% of the total amount of Cu occurs in fulvic-metal complexes. Copper forms stable complexes with humic and fulvic acids (Stevenson and Fitch, 1981). The complexing ability is due to their high oxygen-containing functional groups such as carboxyl, phenolic hydroxyl, and carbonyls of various types (Schnitzer, 1969; Stevenson, 1972). Overall, the greater concentrations of mobile Cu phases observed at the south end of the site may have been due to a lack of uniformly applied or incorporated biosolids, or not enough biosolids/lime applied to raise soil pH and complex excess Cu in Fe/Mn oxide phases. However, if mobile phases were present in greater quantities over the entire site prior to reclamation, then a positive phase shift has occurred towards more immobile Cd phases following reclamation.

Iron

All but the soluble/exchangeable phase (Fig 5 (a)) had two-sided p-values of <0.10. Specifically sorbed/weakly bound, non-crystalline Fe/Mn oxides, and crystalline Fe/Mn oxides/organically complexed Fe concentrations were elevated on the site's south side (Fig 5 (b), (c), and (d)). The residual organically bound Fe concentration was greater on both north and south sides (Fig 5 (e)). Residual inorganic Fe concentration was greatest on the site's north side (Fig 5 (f)). The greatest Fe concentrations were found in crystalline Fe/Mn oxide & organically complexed, residual organic, and residual inorganic phases. As with Cd and Cu, elevated Fe concentrations in mobile phases on the south side of the site may have been due to a lack of uniformly applied or incorporated biosolids, or not enough biosolids/lime applied to raise soil pH and complex excess Fe in relatively immobile phases. However, if mobile phases were present in greater concentrations over the entire site prior to reclamation, then a positive phase shift has occurred towards   more   immobile   Cd   phases   associated   with   reclamation.
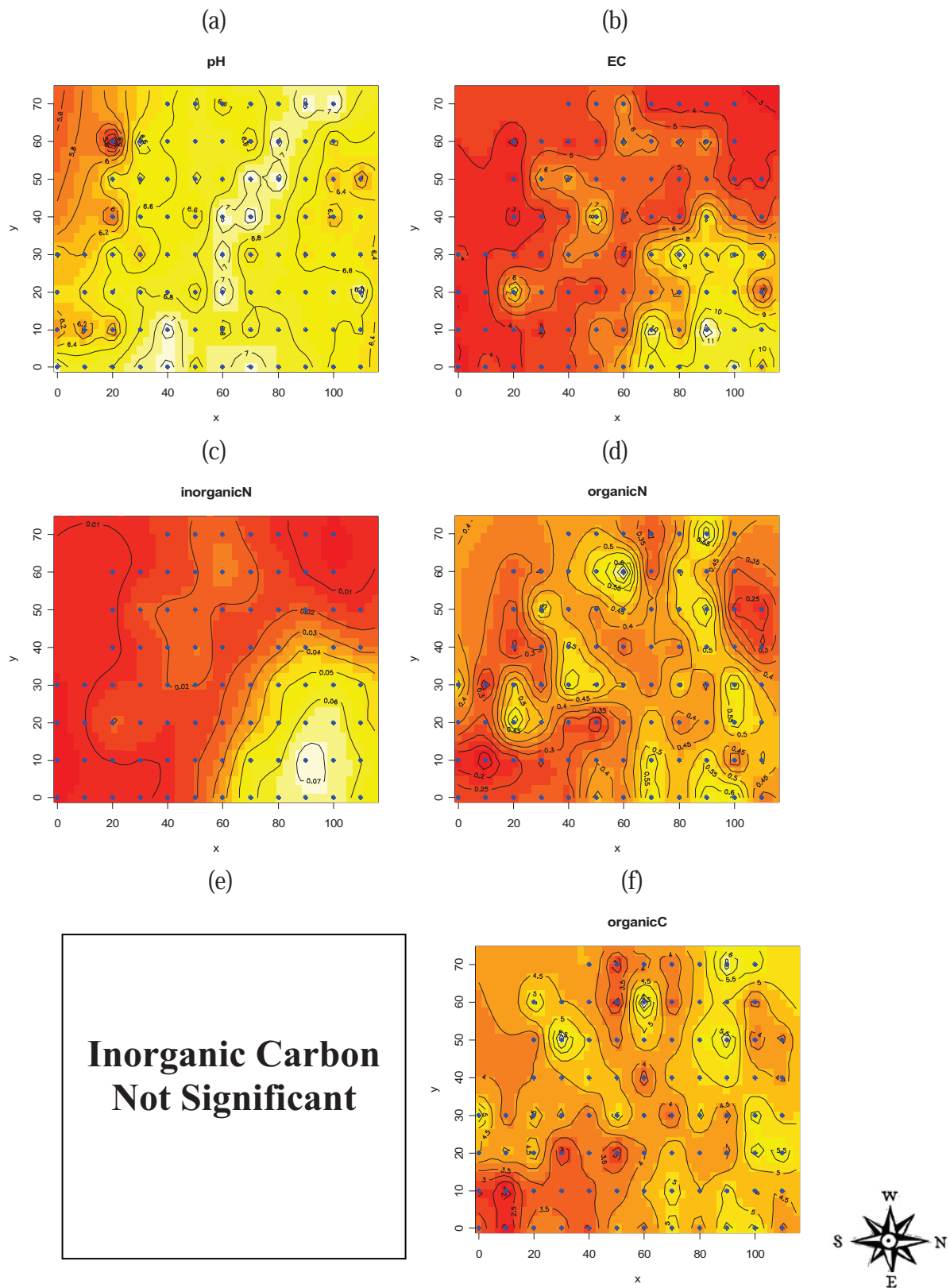
Fig 2: Basic soil characteristics: (a) pH, (b) electrical conductivity, (c) inorganic nitrogen, (d) organic nitrogen, (e) inorganic carbon, and (f) organic carbon. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.
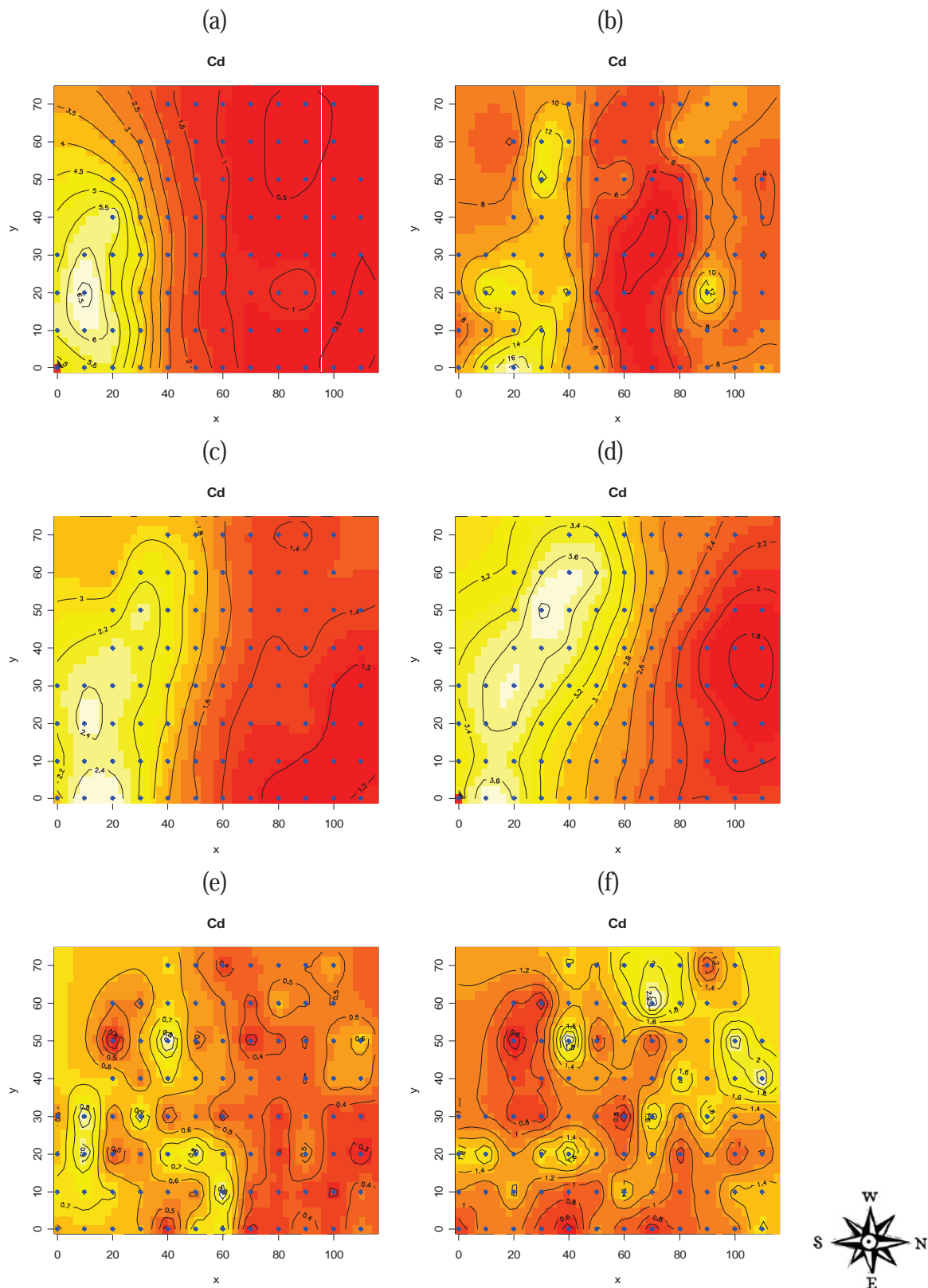
Fig 3: Cadmium associated with: (a) soluble and exchangeable, (b) specifically sorbed/weakly bound, (c) non-crystalline Fe/Mn oxides, (d) crystalline Fe/Mn oxides & organically complexed, (e) residual organic, and (f) residual inorganic phases. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.

Fig 4: Copper associated with: (a) soluble and exchangeable, (b) specifically sorbed/weakly bound, (c) non-crystalline Fe/Mn oxides, (d) crystalline Fe/Mn oxides & organically complexed, (e) residual organic, and (f) residual inorganic phases. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.
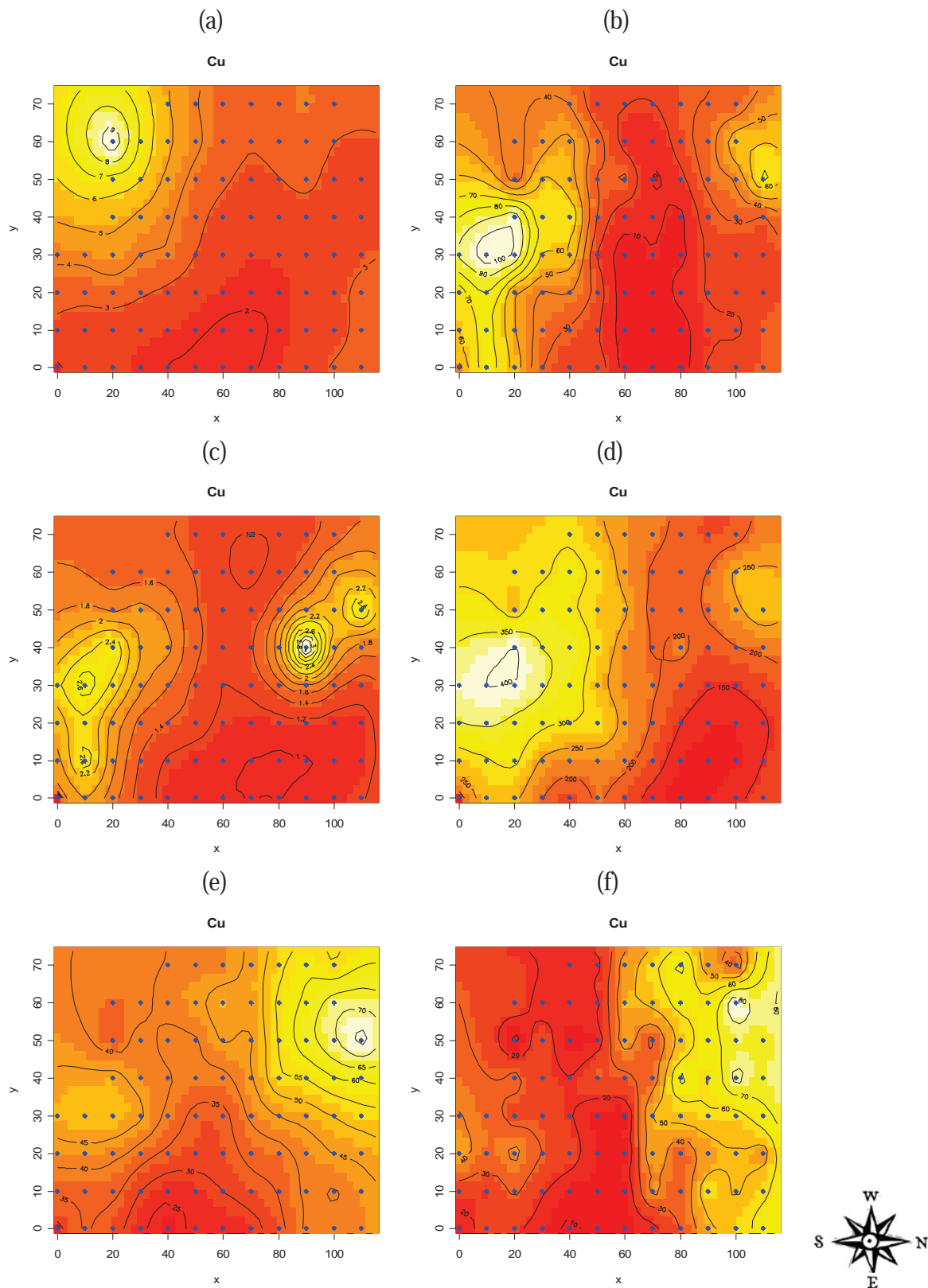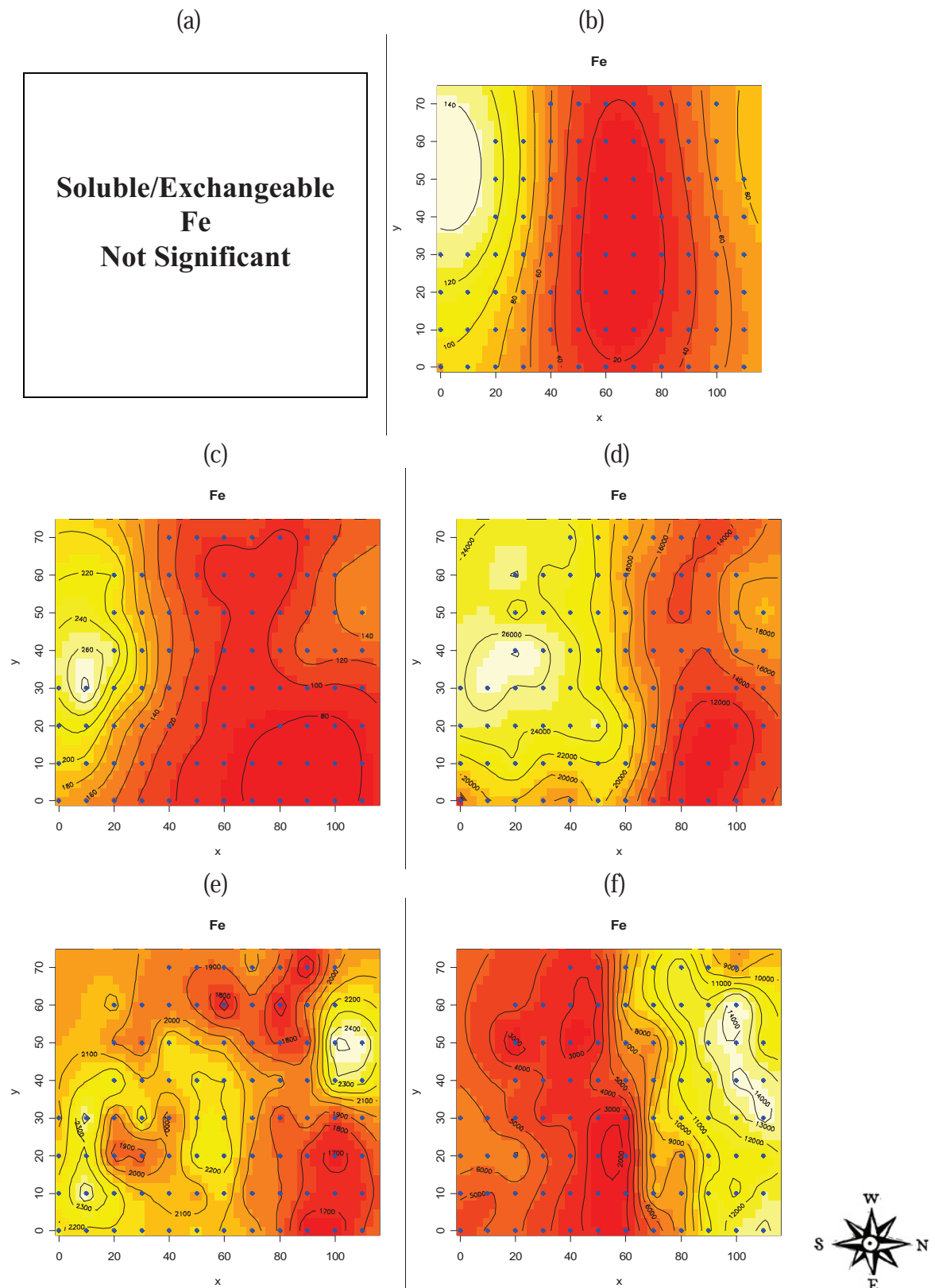
427

Fig 5: Iron associated with: (a) soluble and exchangeable, (b) specifically sorbed/weakly bound, (c) non-crystalline Fe/Mn oxides, (d) crystalline Fe/Mn oxides & organically complexed, (e) residual organic, and (f) residual inorganic phases. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.

428

Lead

All but the soluble/exchangeable phase (Fig 6 (a)) had two-sided p-values of <0.10. The soluble/exchangeable phase concentrations were mostly below detection (data not shown). Specifically sorbed/weakly bound and non-crystalline Fe/Mn oxide associated Pb had slightly higher concentrations on the site's south side (Fig 6 (b) and (c)). Crystalline Fe/Mn oxides/organically complexed Pb concentration was greater on the site's south side (Fig (d)). Residual organic and residual inorganic Pb concentrations were greater on the north side (Fig (e) and (f)). Of all fractions the greatest Pb concentration was found in the crystalline Fe/Mn oxide and organically complexed phase. Soldatini et al. (1976) indicated that OM and clay were the dominant constituents contributing to Pb adsorption in soils. As with other metals, if Pb were originally present in greater quantities as relatively mobile phases, then a significant positive phase shift has occurred towards more immobile Mn phases (i.e. crystalline Fe/Mn oxide and organically complexed phases).

Manganese

All but the soluble/exchangeable phase (Fig 7 (a)) and specifically sorbed/weakly bound phase (Fig 7 (b)) had two-sided p-values of <0.10. These two phases were not affected by reclamation efforts. Non-crystalline Fe/Mn oxide and crystalline Fe/Mn oxides/organically complexed Mn concentrations were elevated on the site's south/west side (Fig 7 (c) and (d)). Residual organic Mn showed a single area on the east/north side of the site with high Mn concentrations (Fig 7 (e)). Residual inorganic Mn concentrations were greatest on the site's north side (Fig 7 (f)). The greatest Mn concentrations were found in the non-crystalline Fe/Mn oxide and crystalline Fe/Mn oxides/organically complexed phases (and at least two to four times greater than both soluble/exchangeable and specifically sorbed/weakly bound phases; data not shown). Shuman (1985) found that most of the total Mn was found in the organic and Mn oxides fractions. As a note, non-crystalline and crystalline Mn oxides can also form coprecipitates with Fe oxides. Manganese availability is also affected by redox conditions, so Mn fractionation may have been influenced by low water levels, a function of sample collection time (October 2006).

Zinc

All phases had two-sided p-values of <0.10. Soluble/exchangeable Zn concentrations were greatest on the site's south side (Fig 8 (a)). Specifically sorbed Zn concentrations were greatest on both the site's north and south sides (Fig 8 (b)). Zinc associated with non-crystalline Fe/Mn oxide and crystalline Fe/Mn oxides/organically complexed phases was greatest on the south side of the contour map (Fig 8 (c) and (d)). Residual organically bound Zn content was greatest on the site's north/west side with some elevated concentrations on the south/east side (Fig 8 (e)). Residual inorganic Zn concentration was greatest on the site's north/west side (Fig 8 (f)). Zinc concentration was uniform across all phases; no single phase dominated. Ramos et al. (1994) found that the distribution of zinc followed the order of Fe/Mn oxides > carbonates ≥ residual > > organic > exchangeable. Zinc complexation increased with the humification of OM (Adriano, 2001). With additions of organic amendments to soils in the form of solid OM (as opposed to soluble OM, such as humic and fulvic acids) in general, tend to shift Zn to more non-bioavailable forms (Shuman, 1999). Since soluble phases primarily dominated the south side of the site, a reduction in biosolids/lime application caused Zn to continue to be more prevalent in mobile phases.

Fig 6: Lead associated with: (a) soluble and exchangeable, (b) specifically sorbed/weakly bound, (c) non-crystalline Fe/Mn oxides, (d) crystalline Fe/Mn oxides & organically complexed, (e) residual organic, and (f) residual inorganic phases. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.

Fig 7: Manganese associated with: (a) soluble and exchangeable, (b) specifically sorbed/weakly bound, (c) non-crystalline Fe/Mn oxides, (d) crystalline Fe/Mn oxides & organically complexed, (e) residual organic, and (f) residual inorganic phases. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.
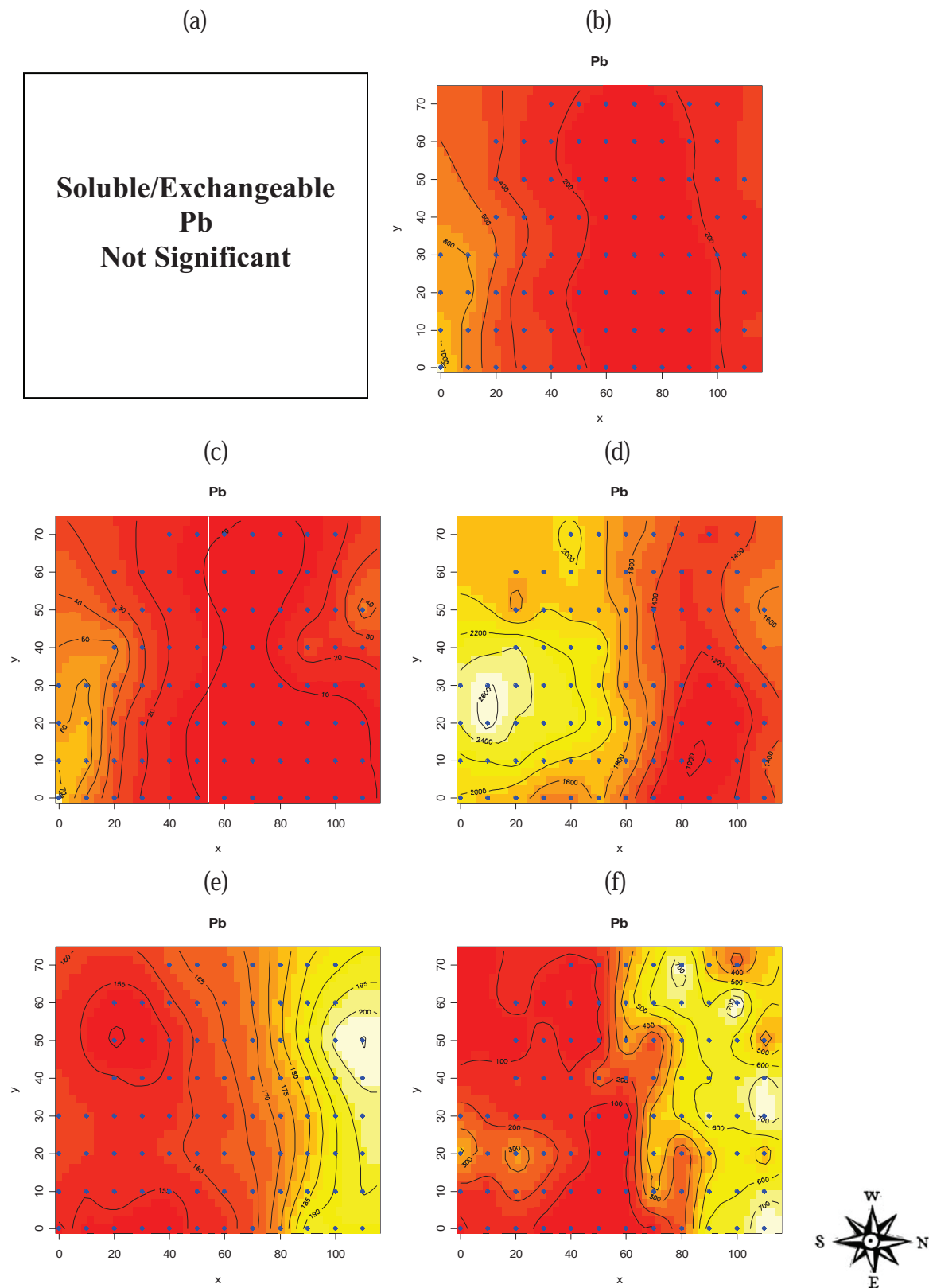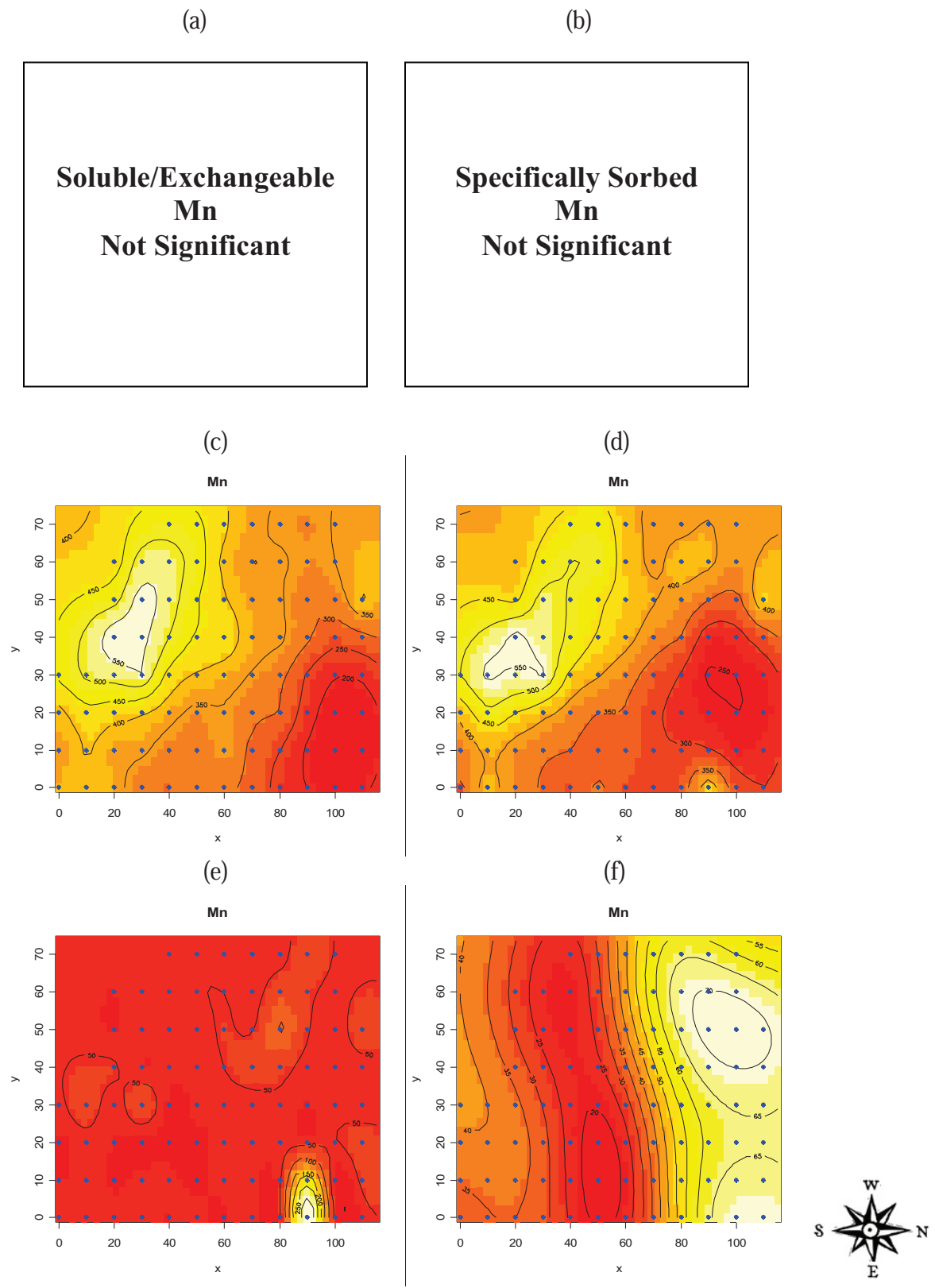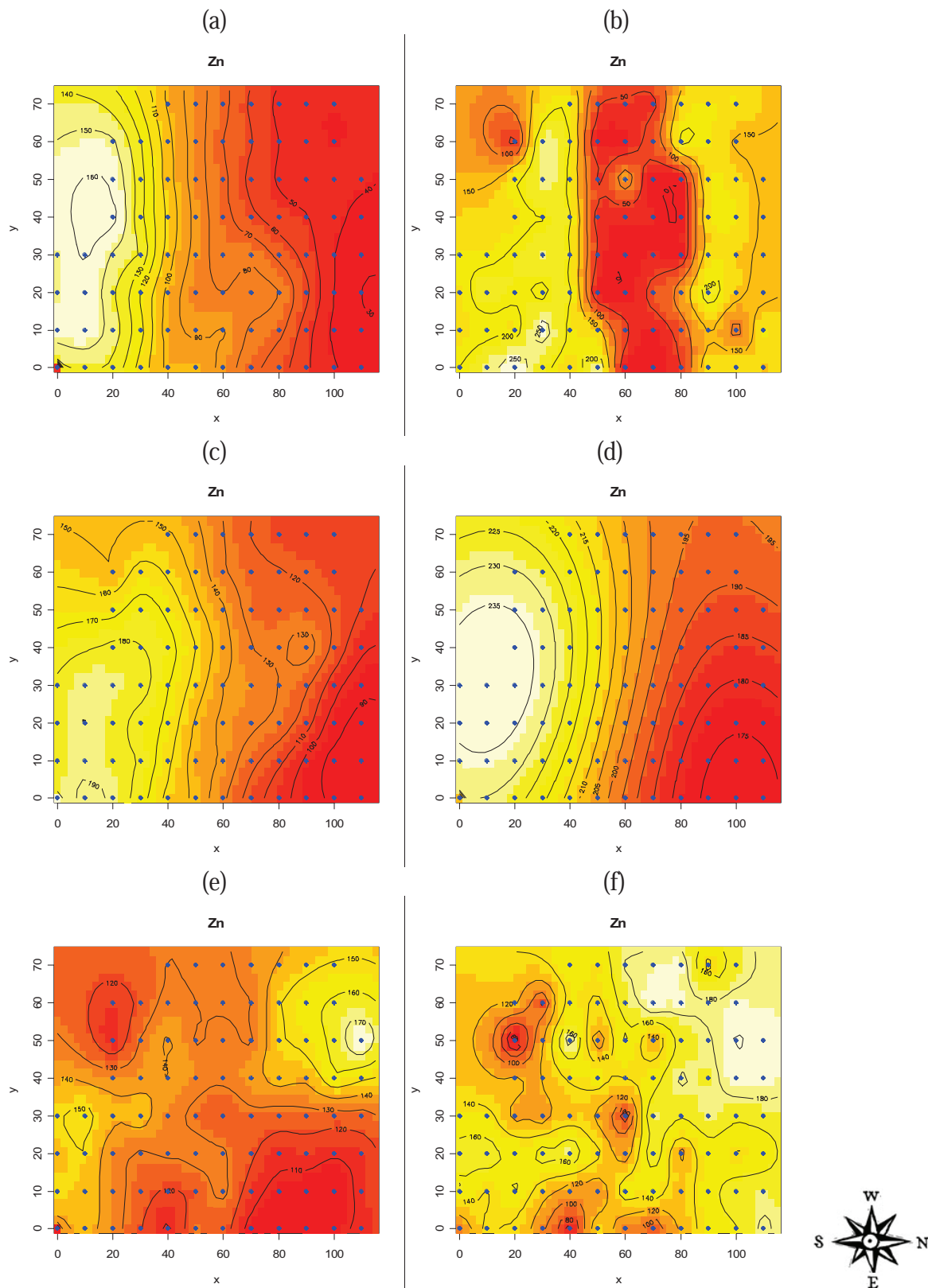
Fig 8: Zinc associated with: (a) soluble and exchangeable, (b) specifically sorbed/weakly bound, (c) non-crystalline Fe/Mn oxides, (d) crystalline Fe/Mn oxides & organically complexed, (e) residual organic, and (f) residual inorganic phases. Darker colors (e.g. red) = relatively low concentration. Lighter colors (e.g. white) = relatively high concentration.

432

Spatial Cross-Correlations: Metal Fractionation Steps vs. Basic Soil Characteristics

Cadmium was negatively correlated with pH, EC, inorganic nitrogen, organic nitrogen, and organic carbon for the first five steps and a positive correlation of step 6 and organic nitrogen and carbon (Table 1 (a)). Inorganic carbon had no effect on any of the steps, assuming $CdCO_3$ was not formed. This could be a function of lime increasing pH, consuming H^+ ions, and thus increasing exchange sites for reaction.

Copper step 1 had negative correlations with pH, EC, and inorganic nitrogen (Table 1 (b)). Step 2 showed negative correlations with pH, EC, inorganic nitrogen, organic nitrogen, and organic carbon. Step 3 had negative correlations with pH, EC, inorganic nitrogen, and organic nitrogen. Step 4 showed a positive correlation with organic carbon and negative correlations with the remaining basic soil characteristics. Step 5 was positively correlated with organic nitrogen and organic carbon, and negatively correlated with inorganic carbon. Step 6 showed positive correlations with EC, inorganic nitrogen, organic nitrogen, and organic nitrogen, and a negative correlation with inorganic carbon.

Iron step 1 had positive correlations with EC, inorganic nitrogen, and organic carbon (Table 1 (c)). Step 2, 3, and 4 had negative correlations with pH, EC, inorganic nitrogen, organic nitrogen, and organic carbon. Inorganic carbon for steps 2 and 4 varied with step 2 being negatively correlated and step 4 being positively correlated. Step 5 had negative correlations with EC, inorganic nitrogen, organic nitrogen, and organic carbon. Step 6 was negatively correlated with inorganic carbon while the rest of the basic parameters were positively correlated. With step 6 (the residual inorganic phase) having positive correlations, one can assume that as pH increased the stable residual mineral phases increased.

Lead and manganese in the first four steps primarily were negatively correlated with the basic soil analysis (Table 1 (d) and (e). Steps 5 and 6 reversed this trend, with Pb and Mn primarily being positively correlated with the basic analysis. This positive correlation was found in the residual organic and residual inorganic phases of the fractionation.

Zinc was primarily negatively correlated with the basic soil analysis in the first five steps, while in step 6 it was positively correlated (Table 1 (f)). Since step 6 had a positive correlation, an assumption can be made that as pH increased residual Zn mineral phases increased.

Table 1.   Cross correlations between basic soil analysis and (a) cadmium, (b) copper, (c) iron, (d) lead, (e) manganese, and (f) zinc steps 1 (soluble/exchangeable), 2 (specifically sorbed/weakly bound), 3 (non-crystalline Fe/Mn oxides), 4 (crystalline Fe/Mn oxides/organically complexed), 5 (residual organic), and 6 (residual inorganic).

(a)

Cd Steps	pH	EC	Inorg N	Org N	Inorg C	Org C
1	-	-	-	-	NS	-
2	-	-	-	-	NS	-
3	-	-	-	-	NS	-
4	-	-	-	-	NS	-
5	-	-	-	-	NS	-
6	NS	NS	NS	+	NS	+

(b)

Cu Steps	pH	EC	Inorg N	Org N	Inorg C	Org C
1	-	-	-	NS	NS	NS
2	-	-	-	-	NS	-
3	-	-	-	-	NS	NS
4	-	-	-	-	+	-
5	NS	NS	NS	+	-	+
6	NS	+	+	+	-	+

(c)

Fe Steps	pH	EC	Inorg N	Org N	Inorg C	Org C
1	NS	+	+	NS	NS	+
2	-	-	-	-	-	-
3	-	-	-	-	NS	-
4	-	-	-	-	+	-
5	NS	-	-	-	NS	-
6	+	+	+	+	-	+

(d)

Pb Steps	pH	EC	Inorg N	Org N	Inorg C	OrgC
1	NS	-	-	NS	NS	NS
2	-	-	-	-	NS	-
3	-	-	-	-	NS	-
4	-	-	-	-	+	-
5	NS	+	+	+	NS	+
6	+	+	+	+	-	+

(e)

Mn Steps	pH	EC	Inorg N	Org N	Inorg C	Org C
1	NS	-	-	NS	NS	NS
2	NS	-	-	NS	NS	NS
3	-	-	-	-	+	-
4	-	-	-	-	+	-
5	NS	+	+	+	NS	+
6	+	+	+	+	-	+

(f)

Zn Steps	pH	EC	Inorg N	Org N	Inorg C	Org C
1	-	-	-	-	NS	-
2	-	-	-	-	-	-
3	-	-	-	-	NS	-
4	-	-	-	-	+	-
5	NS	-	-	-	NS	NS
6	NS	+	+	+	NS	+

CONCLUSIONS

Biosolids are becoming a more sought after tool for reclaiming contaminated mining sites. This study was conducted to determine the effect of biosolids and lime on the reclamation of a heavily contaminated fluvially deposited mine tailings site near Leadville, Colorado. We utilized a sequential trace metal extraction scheme to identify dominant metal pools and to assess bioavailability. Thus, the fractionation of the heavy metals from the site gives important information on the location, behavior, and availability of these metals in the environment. Cadmium was found primarily in the soluble/exchangeable and specifically sorbed/weakly bound phases, potentially plant-available and mobile. Copper was found primarily in organically complexed and residual organic phases, relatively immobile phases. Iron was found primarily in the crystalline Fe/Mn, residual organic, and residual inorganic phases, relatively immobile phases. Of all phases, Pb concentration was greatest in the crystalline Fe/Mn oxides and organically complexed phase, a relatively immobile phase. Manganese was primarily found in relatively immobile non-crystalline and crystalline Mn oxides. Zinc was equally distributed through all six steps.

Overall, the greatest concentration of mobile metal phases was observed at the south end of the site. This finding, as compared to the rest of the site, may have been due to a lack of uniformly applied or incorporated biosolids, or not enough lime applied to raise soil pH and complex excess metals in more immobile phases. If mobile phases were present in greater concentrations over the entire site prior to reclamation, then a positive phase shift has occurred towards more immobile metal phases following reclamation. We are currently conducting research to relate plant species richness, plant metal concentrations/uptake, and microbial community response to reclamation success.

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