Effect of the *Prestige* Oil Spill on Salt Marsh Soils on the Coast of Galicia (Northwestern Spain)

M. L. Andrade,* E. F. Covelo, F. A. Vega, and P. Marcet

ABSTRACT

At four estuarine sites on the coast of Galicia (northwestern Spain), all of which were affected by the *Prestige* oil spill, soil samples were taken from polluted and unpolluted areas and their petroleum hydrocarbon contents, heavy metal contents, and other chemical and physical characteristics were measured. Oil pollution altered both chemical and physical soil properties, aggregating soil particles in plaques, lowering porosity, and increasing resistance to penetration and hydrophobicity. The chromium, nickel, copper, iron, lead, and vanadium contents of polluted soils were between 2 and 2500 times higher than those of their unpolluted counterparts and the background concentrations in Galician coastal sediments. In the cases of Cr, Cu, Ni, Pb, and V, their origin in the polluting oil was corroborated by the high correlation ($r \geq 0.74$) between the concentrations of these metals and the total petroleum hydrocarbon (TPH) content of the polluted soils. Soil redox potentials ranged from −19 to −114 mV in polluted soils and 112 to 164 mV in unpolluted soils, and were negatively correlated with TPH content ($p < 0.01$). The low values in the polluted soils explain why the soluble fractions of their total heavy metal contents were very small (generally less than 3%, and in many cases undetectable).

The oil tanker *Prestige* sprang a leak off Cape Finisterre (Galicia, northwestern Spain) on 13 Nov. 2002. Six days later the ship broke in two and sank 130 nautical miles off the coast. In all, the ship spilled an estimated 64 000 Mg of heavy fuel oil, a material with high nitrogen, sulfur, and heavy metal contents that forms highly viscous, poorly soluble emulsions (Hodgson, 1954; Wedepohl, 2000; Bu-Olayan et al., 1998) in sea water. The spill affected a large part of the Galician coast and coastal waters, and much of the rest of the southern Bay of Biscay. Oil removal efforts have mainly been directed at beaches and, secondarily, rocks and cliffs. This paper concerns the effects of the spill on salt marshes, a type of ecosystem that was also severely affected and where conventional mechanical oil removal methods would wipe out most vegetation.

Marshes, which constitute an important component of river, estuarine, and coastal ecosystems, are extremely sensitive to oil pollution (Gundlach et al., 1977) and can be severely damaged by spills, which block carbon fixation by stifling plant transpiration and, through this mechanism and others, can kill marsh vegetation (Pezeshki et al., 2000). Fuel oil from spills has been known to persist for at least 5 yr in marsh sediments, from which it can be released into the marsh water. This persistence is reflected by high hydrocarbon levels in shellfish inhabiting the polluted marsh or exposed to hydrocarbons released therefrom (Burns and Teal, 1979; Sanders et al., 1980; Maki, 1991; Wade, 1993). To be able to design appropriate recovery strategies, it is essential to gain understanding of the effects of oil pollution on marshes and of their response to such aggressions. The fate of pollution in wetlands differs from that observed in unsaturated soils, in which transport, as well as biodegradation, play a major role (Mackay, 1988): in wetlands, vertical transport through the soil is very slow because of its being almost permanently waterlogged (although the burial of heavy oil under its own weight occurs on a significant scale), and although volatilization of oil spilled on open water is a very significant dispersal mechanism, volatilization from marshes is hindered by the formation of a "composite" of oil and vegetation. The long-term response to oil pollution in marshes depends mainly on the interaction of the oil with the microbial population of the soil, which not only performs biodegradation of the pollutant (Hambrick et al., 1980) but also controls other soil properties and processes that influence the rate at which biodegradation can occur, including the remineralization of nutrients, redox potential (Eh), and pH (Nyman and Patrick, 1995; Nyman, 1999).

Salt marsh soils generally have low bulk densities (because of waterlogging), high organic matter contents (which in many cases now derive not only from the remains of marsh vegetation but also from agricultural and urban waste), and high sulfide contents (Griffin and Rabenhorst, 1989; Fernández Feal, 1999; Marcet et al., 2000; Andrade et al., 2002). These characteristics are not unrelated: the combination of anaerobic conditions and high organic matter content creates an ideal environment for microbial reduction of sulfates to sulfides (Pons and Van Breemen, 1982). Their organic matter content, redox status, and sulfide content play a decisive role in the fate of heavy metals such as those borne in the *Prestige* spill, determining their distribution among dissolved, available, and insoluble forms (Griffin and Rabenhorst, 1989; Gambrell et al., 1991).

The salt marshes of Camariñas and Muxía, and those associated with the beaches of Barizo and Traba Lagoon, are located in estuaries on the stretch of the Galician coast that was most directly affected by the *Prestige* spill, the Costa da Morte (Fig. 1). Most of the soils are classified as tidal marsh soils, and have textures ranging from loamy sand to loam and the high organic matter and sulfide contents that are typical of marsh soils. The predominant vegetation consists of rushes (*Juncus* spp.) at Muxía and Barizo marshes, together with seaside

Department of Vegetable Biology and Soil Science, Ap. 874, 36200 Vigo, Spain. Received 13 Jan. 2004. *Corresponding author (mandrade@uvigo.es).

Published in J. Environ. Qual. 33:2103–2110 (2004).

677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: Eh, redox potential; TPH, total petroleum hydrocarbon.

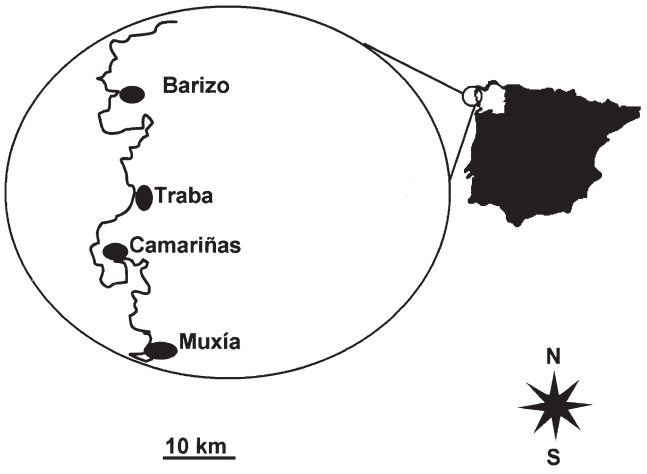

Fig. 1. The study areas.

sandplant [*Honckenya peploides* (L.) Ehrh.] in the latter. At Traba Lagoon beach, St. Augustine grass [*Stenotaphrum secundatum* (Walt.) Kuntze] predominates, together with rushes and common reed [*Phragmites australis* (Cav.) Trin. ex Steud.]. The dominant vegetation at Camariñas salt marsh is sand ryegrass [*Leymus arenarius* (L.) Hochst.], in addition to rushes. Here we report the effects of the spill on the physical and physicochemical properties and hydrocarbon and heavy metal contents of the soils of affected areas of these marshes three months after the spill had occurred.

MATERIALS AND METHODS

To determine whether the spilled oil had undergone changes in metal content before its entrapment in marsh soil, and to predict its biodegradability, five samples of fuel oil were taken for analysis from each of three different sources. Spilled oil was recovered from the open sea in the neighborhood of the *Prestige* by boats on 17 Nov. 2002 (Source 1; the exact positions of recovery were 42°10′48″N 12°0′36″W and 42°12′30″N 12°3′0″W). Oil pats were collected from the surface of beach or marshland at Barizo (Source 2) and Muxía (Source 3) on 24 Feb. 2003, when initial cleaning of the beaches had already been performed. The five samples from each source were pooled and homogenized. The general characteristics of the resulting homogenized samples (one from each source) were determined using the analytical methods listed in Table 1. Their heavy metal contents were determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES) in a PerkinElmer (Wellesley, MA) Optima 4300 DV apparatus following digestion with HNO_3 and H_2O_2 in a Teflon bomb heated in a microwave oven (ASTM Method D 3605; American Society for Testing and Materials, 1995a). For each homogenized sample, the products of three replicate digestion processes were each analyzed in triplicate, and results shown are the means of the nine determinations.

On the same day that the oil pats constituting Sources 2 and 3 were collected, six loose soil samples and six 30-cm soil cores were taken from the top 30 cm of each of five representative polluted areas, and six samples and six cores from each of five representative unpolluted areas, at each of the four marshes studied: Barizo, Traba Lagoon, Camariñas, and Muxía (Fig. 1). Polluted areas were sampled 50 m from the low-water line, and unpolluted (control) areas approximately 200 m from the low-water line; all these soils are Thionic Fluvisols according to the FAO classification (Food and Agriculture Organization, 1998). Loose soil samples were collected using a Model 04.20.SA sampler (Eijkelkamp Agrisearch Equipment, the Netherlands) and were stored in polyethylene bags. Cores were obtained with steel soil sampling rings that were then stored in plastic boxes. Both cores and loose samples were transported to the laboratory in darkness at 4°C. In the laboratory, three of the loose samples from each sampling area were air-dried, passed through a 2-mm-mesh sieve, pooled, and homogenized. Both cores and loose samples were stored in darkness at 4°C until use.

Resistance to penetration and Eh were determined in situ at each sampling area. Resistance to penetration was measured with a hand cone penetrometer by determining the force necessary for it to penetrate to depths of 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 cm (Hartge and Bohne, 1985). The Eh at each of three depths (1, 10, and 20 cm) was measured by inserting polished platinum electrodes to the desired depth and allowing them to equilibrate for 15 min before voltage relative to a calomel electrode was measured with a pH/mV meter; Eh was calculated as the measured voltage plus 244 mV (McKee et al., 1988; Patrick et al., 1996). In each case, measurements were made in triplicate at each sampling area; results presented are the means of the $3 \times 5 = 15$ values obtained for each kind of soil (polluted or unpolluted) in each marsh.

The intrinsic permeability of cores was measured using an air permeameter placed at their head (Bradford, 1986; Corey, 1986), their hydrophobicity using the water drop penetration method of Letey (1969a, 1969b), and their porosity by the method described by Bradford (1986) and Corey (1986). In each case, three cores were used; results presented are the means of the $3 \times 5 = 15$ values obtained for each kind of soil

Table 1. Characteristics of fuel oil from Sources 1, 2, and 3.†

	Sample and sampling site					
	Source 1 (open sea)		Source 2 (Barizo beach)		Source 3 (Muxía marsh)	
Characteristic	Vacuum-dried	Moist	Vacuum-dried	Moist	Vacuum-dried	Moist
Density (15°C), kg m^{-3}‡	977a	988a	979a	988a	977a	982a
Viscosity (50°C), mm^2 s^{-1}§	1 630.18a	18 219.80a	1 273.04b	9 441.55b	1 128.58b	8 826.25b
S, g kg^{-1}¶	28.3a	12.68a	23.2b	9.22b	24.8b	9.21b
C, g kg^{-1}¶	830.22a	371.94a	790.99b	314.66b	790.25b	293.49c
N, g kg^{-1}¶	4.2a	2.1c	3.7b	1.6e	4.6a	2.4c
H_2O, % (v/v)#		55.20a		54.26a		55.20a
Ashes, g kg^{-1}††		4.23b		1.55c		5.17a

† For each kind of sample (wet or vacuum-dried), values of a parameter followed by a different letter differ significantly at the 0.05 probability level.
‡ Determined according to ASTM Method D 1998 (American Society for Testing and Materials, 1995a).
§ Determined according to ASTM Method D 445 (American Society for Testing and Materials, 1995a).
¶ Determined according to ASTM Method D 4239 C (American Society for Testing and Materials, 1995b).
# Determined according to ASTM Method D 95 (American Society for Testing and Materials, 1995a).
†† Determined according to ASTM Method D 482 (American Society for Testing and Materials, 1995a).

(polluted or unpolluted) in each marsh. Porosity was also determined (by the same method) for unaltered samples of the compact soil "crusts" described below under Results and Discussion.

The sub-2-mm soil fractions obtained as described above were used for potentiometric measurement of soil pH, for assaying organic matter content per Walkley and Black (1934), and for determination of particle size distribution by the Bouyoucos hydrometer method as described by Day (1965). In each case, three subsamples of the corresponding homogenized pooled sample were taken and each was analyzed in triplicate; results presented are the means of the $3 \times 3 \times 5 = 45$ values obtained for each kind of soil (polluted or unpolluted) in each marsh.

Dissolved heavy metal contents (Cr, Cu, Fe, Ni, Pb, and V) were extracted with acidified 0.1 *M* $CaCl_2$ solution (Houba et al., 2000), available heavy metal contents with DTPA (diethylenetriaminepentaacetic acid; Lindsay and Norwell, 1978), and total heavy metal contents with a 1:3:3 (v/v/v) mixture of nitric, hydrochloric, and hydrofluoric acids in a Teflon bomb heated in a microwave oven (Marcet Miramontes et al., 1997); these extractions were not sequential, each extract being obtained directly from a soil sample stored in darkness at 4°C. In each case, the Cr, Cu, Fe, Ni, Pb, and V contents of the extract in question were determined by ICP–OES (Marcet Miramontes et al., 1997) in the same apparatus as for the samples from Sources 1, 2, 3.

The overall accuracy and precision of the analytical procedure for total heavy metal contents (including extraction) were verified according to Marcet Miramontes et al. (1997) by analyzing the marine sediment reference material MESS-3 (from the Marine Analytical Chemistry Standards Program of the Canadian National Research Council). Material MESS-3 is an estuarine sediment with low to medium metal concentrations, making it suitable for control of analyses of Galician salt marsh samples. Our measurements differed from the certified values by between 2.9% (Cr) and 11.8% (Pb), with standard deviations between 1.4 (V) and 3.6 (Pb) times greater than the certified uncertainty (Table 2).

Total petroleum hydrocarbon (TPH) content was determined per ISO/TR11046(E) (International Organization for Standardization, 1994), the method proposed by Referentie Informatiemodel voor Ziekenhuisapotheken (1980, 1987), Pennings (1987), and Weisman (1998), using soil samples stored in darkness at 4°C. Subsamples were dried chemically over a hygroscopic salt, ground, and extracted with 1,1,2-trichloro-1,2,2-trifluoroethane. The extract was stirred with magnesium silicate (to remove polar organic compounds) and then filtered. Hexane was added, and the mixture was analyzed by gas chromatography using a flame ionization detector and, as external standard, a mixture of *n*-alkanes with between 6 and 36 carbons (Weisman, 1998).

The data were statistically analyzed and the least significant differences (LSD) at the 5% level used to separate means. The relationship between the different variables was evaluated by a simple correlation and regression analysis (Neter et al., 1996).

Table 2. Measured and certified concentrations of heavy metals in reference material MESS-3 (means ± standard deviations; $n = 10$).

Metal	Certified value	Analyzed value
	mg kg^{-1}	
Cr	105 ± 4	108 ± 8
Cu	33.9 ± 1.6	31 ± 5
Ni	46.9 ± 2.6	42.4 ± 6
Pb	21.1 ± 0.7	23.6 ± 2.5
V	243 ± 10	232 ± 14
Zn	159 ± 8	161 ± 5

RESULTS AND DISCUSSION

Characteristics of the Fuel Oil

Table 1 lists the general characteristics of the samples of fuel oil taken at sea and in two of the marshes studied (Sources 1, 2, and 3), and Fig. 2 shows their Cd, Co, Hg, Sn, Cr, Mn, Mo, Cu, Pb, Fe, Ni, and V contents. The metals present in lowest concentration (<0.2 mg kg^{-1}) were Cd, Co, Hg, and Sn, for none of which were there any significant differences between the three sources of samples. Nor did the sources differ with regard to sample Mo and V contents, but they did differ slightly with respect to Mn, Pb, Fe, and Ni, and more substantially with respect to Cu and Cr, with the Cu content of samples from Barizo being about double that of samples from the other sources and the Cr content of samples from Muxía being almost 20 times that of

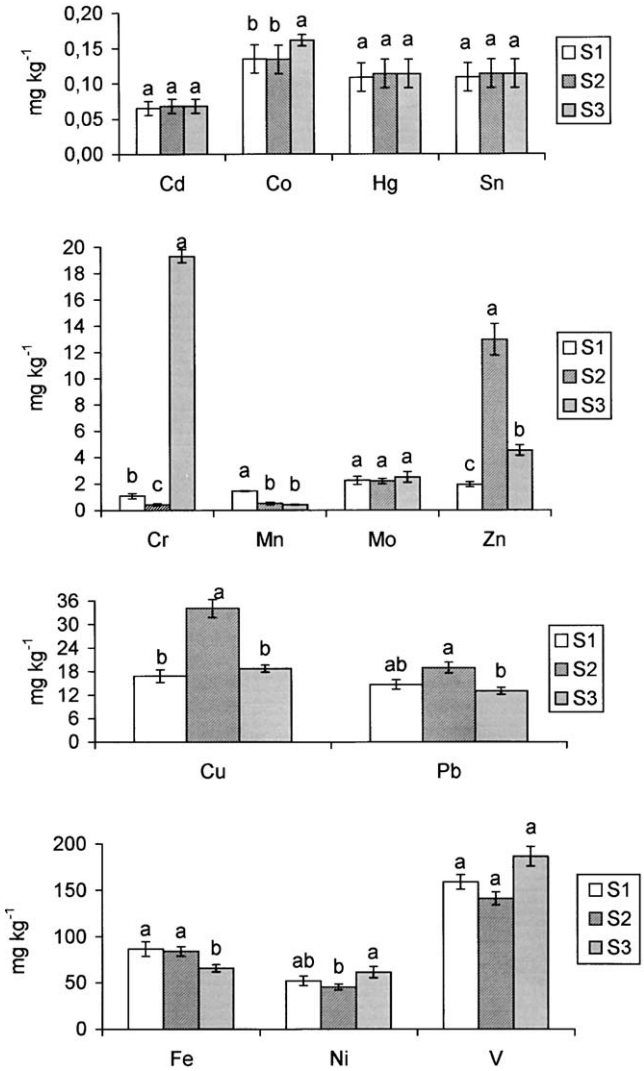

Fig. 2. Heavy metal contents of fuel oil from Sources 1, 2, and 3. For each element, bars labeled with different letters show values that differ significantly at the 0.05 probability level according to Duncan's multiple range test.

samples from the open sea or Barizo. The metals present in greatest concentrations were V (160–190 mg kg^{-1}), followed by Fe and Ni (50–90 mg kg^{-1}) and by the highly toxic elements Cu and Pb (15–35 mg kg^{-1}); except for Pb, all these metals are released very slowly from fuel oil because they are complexed by porphyrins (Roscupp and Bowman, 1967).

The ratio between the concentrations of V and Ni in crude oil is considered to reflect the ease with which the oil can be biodegraded: the larger the ratio, the easier is biodegradation (Louda and Baker, 1986).

The three sources sampled in this work (Sources 1, 2, 3) afforded samples with very similar V to Ni ratios of 3.04, 3.10, and 3.03, respectively, showing that all three are in principle moderately degradable and that, in keeping with the V and Ni concentration results noted above, the different histories of these oils between being spilled and collected had not led to markedly different degrees of biodegradation.

Vanadium and Ni are mainly present in crude oils in the form of metalloporphyrins. Because Ni porphyrins have a lower intrinsic activity than V porphyrins, Ni is more evenly distributed throughout crude oil (Roscupp and Bowman, 1967); however, a further Ni fraction is present in the form of inorganic salts. There is no corresponding V salt fraction, so the majority of the V content of a crude oil sample is associated with porphyrins. As a result, V is more strongly bound within the crude oil as V porphyrins are relatively stable and only release V when decomposed. The use of V to Ni ratios as measures of crude oil degradation is based on these findings (Stencel and Jaffe, 1998). The V to Ni ratio of a crude oil varies according to the origin of the oil, with typical values ranging between 1 and 10 (Louda and Baker, 1986; Fan et al., 2002).

Effects on the Salt Marshes and their Soils

The marsh with by far the most affected soil was Barizo, with a TPH content of 92 g kg^{-1} (Table 3). The affected soils at Traba Lagoon and Camariñas both had TPH contents between 7 and 8 g kg^{-1}, and that of Muxía marsh a content of 1.7 g kg^{-1}. The TPH components were virtually absent from the control soils, which all had TPH contents less than 0.05 g kg^{-1}.

In the areas of marsh affected by the spill, fuel oil had impregnated the roots and lower stems of the rushes constituting the predominant vegetation, "gluing" soil particles to the roots and the stems to one another (Fig. 3). These areas exhibited, on or just below their surface, a compact crust of low porosity (0.20–0.36 m^3 m^{-3}), between 1 and 12 cm thick, that was traversed by cracks 0.3 to 1.0 cm wide. Its color ranged from black (7.5YR2/0) at Barizo (Fig. 3), where it was responsible for the high resistance to penetration of the affected soil, greater than 14 g cm^{-2} (Table 3); through various shades of gray at Camariñas (10YR5/1, 10YR4/1) and Muxía (10YR5/2) (Fig. 3), where the crust was thinner and offered rather less resistance to penetration (between 1 and 4 g cm^{-3}); to yellowish brown (10YR5/8) at Traba Lagoon (Fig. 3), where penetrability was again about 4 g cm^{-2} (in no control soil did resistance to penetration exceed 0.33 g cm^{-2}). The crust was composed of aggregates of fine material agglutinated by the oil, which in coating the finer particles will have facilitated their entry and permanence in the larger pores and channels, "gluing" larger particles together and thus reducing porosity and permeability and increasing resistance to penetration, whereas under normal circumstances the particles of sandy salt marsh soils reorganize during every cycle of wetting and drying and do not cohere, resulting in very low resistance to penetration (Marley and Hoag, 1986; Andrade et al., 2002). The formation of this crust did not alter gross particle size distributions, with the proportions of sand, silt, and clay being the same in polluted as unpolluted soils (78.4, 13.9, and 7.7%, respectively, at Barizo; 87.9, 9.8, and 2.3% at Traba Lagoon; 47.8, 33.8, and 18.4% at Camariñas; and 85.1, 11.7, and 3.2% at Muxía).

Polluted soils differed significantly from their unpolluted counterparts ($p < 0.05$) in hydrophobicity, Eh, and intrinsic permeability as well as in porosity, resistance to penetration, and TPH content (Table 3). Average water drop penetration time (the measure of hydrophobicity) ranged from 5 to 12 s among the unpolluted soils and from 6 min to more than 6 h among the polluted soils,

Table 3. Effect of the *Prestige* oil spill on the soil properties and soil total petroleum hydrocarbon (TPH) content for soils affected by the oil spill and control soils.†

	Barizo beach		Traba Lagoon beach		Camariñas marsh		Muxía marsh	
	Affected	Control	Affected	Control	Affected	Control	Affected	Control
Sand, %‡	78.4b	78.4b	87.9a	87.9a	47.8c	47.8c	85.1ab	85.1ab
Silt, %‡	13.9a	13.9a	9.8c	9.8c	33.8a	33.8a	11.7bc	11.7bc
Clay, %‡	7.7b	7.7b	2.3d	2.3d	18.4a	18.4a	3.2c	3.2c
Porosity, m^3 m^{-3}§	0.26d	0.57a	0.32c	0.59a	0.34c	0.49b	0.41b	0.59a
Hydrophobicity, time§	6 h 12 min (a)	5 s (f)	51 min 13 s (b)	5 s (e)	39 min 13 s (c)	12 s (e)	6 min (d)	5 s (f)
Resistance to penetration, g cm^{-2}§	14.65a	0.25e	4.16b	0.26e	3.82c	0.33e	1.31d	0.26e
Intrinsic permeability, m^2§	1.18×10^{-8}c	1.8×10^{-5}a	4.90×10^{-8}d	1.7×10^{-5}a	3.16×10^{-8}c	1.8×10^{-6}b	1.21×10^{-8}c	1.7×10^{-5}a
pH‡	7.6b	7.2bc	8.1ab	7bc	5.92d	6.8c	8.7a	7bc
Redox potential (Eh), mV§	−114f	112b	−58e	162a	−24d	116b	−19c	164a
Organic matter, g kg^{-1}‡	129.7c	10.3e	8.3f	3.4g	212.8a	162.0b	18.3d	3.5g
TPH, g kg^{-1}†	92.34a	0.04d	7.66b	0.02de	7.24b	0.04d	1.71c	0.01e

† Values followed by different letters in each row differ significantly at the 0.05 probability level.
‡ Means of 45 analyses (three replicate analyses of each of three replicate samples for each of five sampling areas).
§ Means of 15 analyses (three samples from or replicate measurements at each of five sampling areas).

and like resistance to penetration exhibited very close positive correlation with TPH content (Table 4). Average Eh was always positive in control soils (112–164 mV), and always negative in polluted soils, in which it ranged from −19 mV at Muxía to −114 mV at Barizo; like porosity, it exhibited significant negative correlation

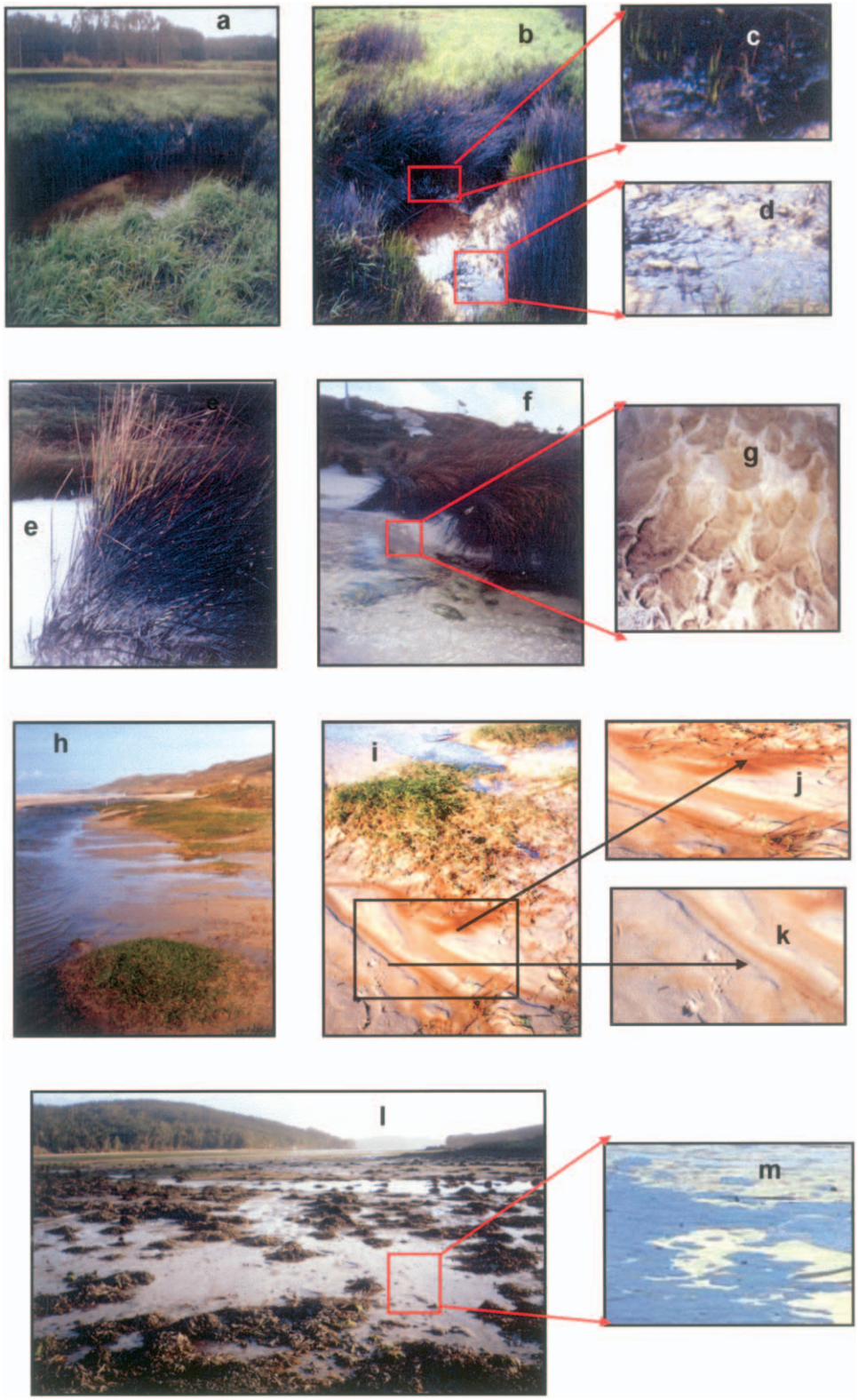

Fig. 3. Affected areas of the marshes studied. (a–d) Barizo: (a) general view, (b) closer view of polluted soil, and (c and d) close-ups of black crusts. (e–g) Muxía: (e) general view, (f) closer view of polluted soil, and (g) close-up of greyish-brown crust. (h–k) Traba Lagoon: (h) general view, (i) closer view of polluted soil, and (j and k) close-ups of yellowish-brown crusts. (l and m) Camariñas: (l) general view and (m) close-up of greyish crusts.

Table 4. Pearson correlations among properties of polluted and unpolluted marsh soils.

	Porosity	Hydrophobicity	Resistance to penetration	Intrinsic permeability	Eh†	TPH‡	Total Cr	Total Cu	Total Fe	Total Ni	Total Pb	Total V
Porosity	1	−0.65**	−0.77**	0.86**	0.95**	−0.62**	−0.90**	−0.93**	−0.39	−0.65**	−0.87**	−0.90**
Hydrophobicity	−0.65**	1	0.98**	−0.39	−0.67**	0.99**	0.83**	0.77**	0.45*	0.95**	0.92**	0.77**
Resistance to penetration	−0.77**	0.98**	1	−0.51*	−0.79**	0.97**	0.91**	0.86**	0.42*	0.94**	0.97**	0.87**
Intrinsic permeability	0.86**	−0.39	−0.51*	1	0.82**	−0.37	−0.66**	−0.73**	−0.41*	−0.43*	−0.64**	−0.65**
Eh	0.95**	−0.67**	−0.79**	0.82**	1	−0.65**	−0.90**	−0.95**	−0.36	−0.67**	−0.89**	−0.86**
TPH	−0.62**	0.99**	0.97**	−0.37	−0.65**	1	0.79**	0.75**	0.39	0.93**	0.91**	0.74**
Total Cr	−0.90**	0.83**	0.91**	−0.66**	−0.90**	0.79**	1	0.92**	0.50*	0.86**	0.93**	0.98**
Total Cu	−0.93**	0.77**	0.86**	−0.73**	−0.95**	0.75**	0.92**	1	0.40	0.75**	0.93**	0.90**
Total Fe	−0.39	0.45	0.42*	−0.41*	−0.36	0.39	0.50*	0.40	1	0.64**	0.36	0.39
Total Ni	−0.65**	0.95**	0.94**	−0.43*	−0.67**	0.93**	0.86**	0.75**	0.64**	1	0.87**	0.78**
Total Pb	−0.87**	0.92**	0.97**	−0.64**	−0.89**	0.91**	0.93**	0.93**	0.36	0.87**	1	0.91**
Total V	−0.90**	0.77**	0.87**	−0.64**	−0.89**	0.74**	0.98**	0.90**	0.39	0.78**	0.91**	1

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
† Redox potential.
‡ Total petroleum hydrocarbon content.

with TPH. Average intrinsic permeability was of the order of 10^{-8} m^2 in polluted soils, compared with 10^{-5} or 10^{-6} m^2 in control soils, but did not correlate significantly with TPH at the $p = 0.05$ significance level.

Polluted soils had significantly higher values than control soils ($p < 0.05$) with respect to total Cr, Cu, Fe, Pb, and V contents and, except at Muxía, total Ni content (Table 5). The heavy metal concentrations found in the polluted soils also exceeded the average concentrations in other unpolluted Galician coastal sediments (Barreiro et al., 1988, 1994; Marcet Miramontes et al., 1997; Fernández Feal, 1999; Carballeira et al., 1997, 2000; Marcet et al., 2000; Andrade et al., 2004) and in the parent materials (Paz González et al., 2000). The highest levels were in all cases except Fe found at Barizo. The differences between Barizo and the other marshes were much less than in the case of TPH content. The origin of these heavy metals in the polluting oil was corroborated by there being significant positive correlation with TPH content ($r \geq 0.74$, $p < 0.01$) in all cases except Fe, and also significant mutual correlation ($r \geq 0.75$, $p < 0.01$) among total Cr, Cu, Ni, Pb, and V levels (Table 4).

Except for Fe, and for Cr at Camariñas, none of the metals studied were detectable in $CaCl_2$ extracts of soil samples. The DPTA-extractable metal contents were likewise low in relative terms, always being less than 3.33% of total contents except in polluted soil from Camariñas, in which 6.5% of total Pb and 10% of total Ni were DPTA-extractable. The predominance of insoluble forms is attributable to the low Eh values of these soils, and hence partly, in the case of the polluted soils, to their TPH contents. This insolubility will also no doubt have contributed to the close negative correlation between Eh and total Cr, Cu, Ni, Pb, and V contents (Table 4) and hence to the correlation between these

Table 5. Heavy metal contents of marsh soils affected by the oil spill and control soils.†

	Barizo beach		Traba Lagoon beach		Camariñas marsh		Muxía marsh	
Metal	**Affected**	**Control**	**Affected**	**Control**	**Affected**	**Control**	**Affected**	**Control**
	mg kg^{-1}							
	Total dissolved							
Cr	ND‡	ND	ND	ND	0.11a‡	ND	ND	ND
Cu	ND	ND	ND	ND	ND	ND	ND	ND
Fe	0.08c	0.01d	0.008f	0.002e	14.93a	1.2b	0.03cd	0.01d
Ni	ND	ND	ND	ND	ND	ND	ND	ND
Pb	ND	ND	ND	ND	ND	ND	ND	ND
V	ND	ND	ND	ND	ND	ND	ND	ND
	DTPA-extractable							
Cr	ND	ND	ND	ND	ND	ND	ND	ND
Cu	0.04bc	0.01c	ND	ND	0.31a	0.06bc	0.09b	0.01c
Fe	143.33b	4.5e	9.34d	1.3f	408.33a	8.7d	14.46c	3.8ef
Ni	0.79b	0.02c	ND	ND	1.05a	0.04c	ND	ND
Pb	1.12a	0.02c	ND	ND	1.02a	0.04c	0.32b	ND
V	0.14b	ND	0.04c	ND	0.34a	ND	0.03c	ND
	Total content							
Cr	30.25a	2.2e	17.1c	1.1ef	20.05b	0.8f	6.5d	0.6f
Cu	43.88a	16d	32b	12e	27.38b	14de	25c	4f
Fe	9 332.88	6 518	432.88	314	12 320.38b	8 144	2 382.88c	832
Ni	24.88a	0.01e	15.63b	2d	10.5c	4d	0.01e	ND
Pb	47.38a	2e	21.38b	2e	15.63bc	4d	12.88c	0.8f
V	58.25a	0.8d	40b	0.3e	38b	0.5de	5.5c	0.2e

† Values are means of 15 analyses (three replicate samples for each of five sampling sites). Values followed by different letters in each row differ significantly at the 0.05 probability level.
‡ Not detectable. Detection limits: Cr, 0.005; Cu, 0.004; Fe, 0.005; Ni, 0.006; Pb, 0.014; and V, 0.005 mg kg^{-1}.

total concentrations and TPH, since it will have prevented these metals from being lost through mobilization.

No significant relationship was found between heavy metal contents and particle size or organic matter content.

CONCLUSIONS

The oil reaching the study areas within three months of the spill had in general not undergone changes in metal contents reflecting significant differences in metal mobilization. Its V to Ni ratio suggested moderate biodegradability.

As expected, the degree to which the study areas had been affected, as reflected by the TPH contents of the polluted soils, differed widely. However, all the polluted soils exhibited, as the main macroscopic effect of the pollution, a dark, compact crust with significantly lower porosity and greater resistance to penetration than those of unpolluted soils at the same sites. Pollution also significantly lowered Eh and intrinsic permeability, raised hydrophobicity, and increased between 2- and 2500-fold the concentrations of Cr, Cu, Fe, Pb, V, and Ni (except the Ni concentrations in the least polluted soil). The lowering of Eh will have contributed to these heavy metals being found almost exclusively in insoluble forms.

Because of the vulnerability of the vegetation of these marshes to mechanical oil removal methods, cleanup procedures should concentrate on enhancing the biodegradation of the oil. The advantages of bioremediation must nevertheless be balanced against the prospect of its releasing high concentrations of toxic heavy metals into the ecosystem, and in considering costs and benefits it must also be kept in mind that release of heavy metals could also be induced by changes in soil acidity.

REFERENCES

American Society for Testing and Materials. 1995a. ASTM Methods D 1998, 95, 445, 3605, and 482. *In* Annual book of ASTM standards. Section 5. Petroleum products, lubricants, and fossil fuels. 05.01. Petroleum products and lubricants (I). ASTM, West Conshohocken, PA.

American Society for Testing and Materials. 1995b. ASTM Method D 4239 C. *In* Annual book of ASTM standards. Section 5. Petroleum products, lubricants, and fossil fuels. 05.02. Petroleum products and lubricants (II). ASTM, West Conshohocken, PA.

Andrade, L., P. Marcet, L. Fernández Feal, C. Fernández Feal, and E. Fernández Covelo. 2004. Impact of the *Prestige* oil spill on marsh soils: Heavy metal contribution in Villarrube and Lires marshes (Galicia, Spain). Cienc. Mar. (in press).

Andrade, L., M.L. Reyzábal, P. Marcet, and M.J. Montero. 2002. Industrial impact on marsh ecosystem at the Bahía Blanca Ría (Argentina). J. Environ. Qual. 31:532–538.

Barreiro, R., A. Carballeira, and C. Real. 1988. Metales pesados en los sedimentos de cinco sistemas de Ría (Ferrol, Burgo, Arousa, Pontevedra y Vigo). (In Spanish, with English abstract.) Thalassas 6:61–70.

Barreiro, R., C. Real, and A. Carballeira. 1994. Heavy metals in sediment cores from NW-Spain estuary. Bull. Environ. Contam. Toxicol. 53:368–373.

Bradford, J.M. 1986. Penetrability. p. 463–477. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Bu-Olayan, A.H., M.N.V. Subrahmanyam, M. Al-Sarawi, and B.V. Thomas. 1998. Effects of the Gulf War oil spill in relation to trace metals in water, particulate matter, and PAHs from the Kuwait Coast. Environ. Int. 24:789–797.

Burns, K.A., and J.M. Teal. 1979. The West Falmouth oil spill: Hydrocarbons in the salt marsh ecosystem. Estuarine Coastal Mar. Sci. 8:349–360.

Carballeira, A., E. Carral, X. Puente, and R. Villares. 2000. Regional-scale monitoring of coastal contamination. Nutrients and heavy metal in estuarine sediments and organisms on the coast of Galicia (northwest Spain). Rev. Int. Contam. Ambiental 13:534–572.

Carballeira, A., E. Carral, X.M. Puente, and R. Villares. 1997. Estado de conservación de la costa de Galicia. Univ. de Santiago de Compostela, Spain.

Corey, A.T. 1986. Air permeability. p. 1121–1136. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Day, P.R. 1965. Particle size analysis. p. 545–567. *In* C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark (ed.) Methods of soil analysis. Part 1. Agron. Monogr. 9. ASA, Madison, WI.

Fan, T., J.X. Wang, and J.S. Buckley. 2002. Evaluating crude oils by SARA analysis. Paper SPE 75228. *In* SPE/DOE Symp. on Improved Oil Recovery, Tulsa, OK. 15–17 Apr. 2002. IOR, Tulsa, OK.

Fernández Feal, M.L. 1999. Contribución al estudio de las marismas de los ríos Xubia y Ferrerías. Ph.D. thesis. Univ. de La Coruña, Spain.

Food and Agriculture Organization. 1998. World reference base for soil resources. World Soil Resour. Rep. 84. FAO, Rome.

Gambrell, R.P., J.B. Wiesepape, W.H. Patrick, and M.C. Duff. 1991. The effects of pH, redox and salinity on metal release from a contaminated sediment. Water Air Soil Pollut. 57/58:359–367.

Griffin, T.M., and M.C. Rabenhorst. 1989. Process and rates of pedogenesis in some Maryland tidal marsh soils. Soil Sci. Soc. Am. J. 53:862–870.

Gundlach, E.R., M.O. Hayes, C.H. Ruby, L.G. Ward, A.E. Blount, I.A. Fisher, and R.J. Stein. 1977. Some guidelines for oil-spill control in coastal environments, based on field studies of four oil spills. p. 98–118. *In* L.T. McCarthy, Jr., G.P. Lindblom, and H.F. Walter (ed.) Chemical dispersants for the control of oil spills. ASTM STP 659. ASTM, West Conshohocken, PA.

Hambrick, G.A. III, R.D. DeLaune, and W.H. Patrick, Jr. 1980. Effect of estuarine sediment pH and oxidation-reduction potential on microbial hydrocarbon degradation. Appl. Environ. Microbiol. 40: 365–369.

Hartge, K.H., and H. Bohne. 1985. Penetrometer measurements for screening soil physical variability. Soil Tillage Res. 5:343–350.

Hodgson, G.W. 1954. Vanadium, nickel and iron trace metals in crude oils of western Canada. AAPG Bull. 38:2537–2554.

Houba, V.J.G., E.J.M. Temminghoff, G.A. Gaikhorst, and W. van Vark. 2000. Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. Commun. Soil Sci. Plant Anal. 31:1299–1396.

International Organization for Standardization. 1994. ISO/TR 11046(E). p. 105–111. *In* ISO standard compendium. Environmental soil quality. General aspects. Chemical and physical methods of analysis, biological methods of Analysis. ISO, Geneva.

Letey, J. 1969a. Water drop penetration time. p. 6–10. *In* L.F. DeBano and J. Letey (ed.) Proc. Symp. on Water Repellent Soils, Riverside, CA. 6–10 May 1968. Univ. of California, Riverside.

Letey, J. 1969b. Measurement of contact angle, water drop penetration time and critical surface tension. 43–47. *In* L.F. DeBano and J. Letey (ed.) Proc. Symp. on Water Repellent Soils, Riverside, CA. 6–10 May 1968. Univ. of California, Riverside.

Lindsay, W.L., and W.A. Norwell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42:421–428.

Louda, J.W., and E.W. Baker. 1986. The biochemistry of chlorophyll. p. 107–126. *In* M.L. Sohn (ed.) Organic marine geochemistry. ACS Symp. Ser. 305. Am. Chem. Soc., Washington, DC.

Mackay, D. 1988. The chemistry and modeling of soil contaminated with petroleum. p. 5–18. *In* E.J. Calabrese and P.T. Kostecki (ed.) Soil contaminated with petroleum: Environmental and public health effects. Wiley-Interscience, New York.

Maki, A.W. 1991. The Exxon Valdez oil spill: Initial environmental impact assessment. Environ. Sci. Technol. 25:24–29.

Marcet, P., M.L. Fernández Feal, M.L. Andrade Couce, and M.J. Montero Vilariño. 2000. Efecto de la influencia antrópica sobre

las características fisicoquímicas de dos suelos de marisma. (In Spanish, with English abstract.) Edafología 7(3):11–19.

Marcet Miramontes, P., M.L. Andrade Couce, and M.J. Montero Vilariño. 1997. Efficacité d'une methode de digestion par microondes pour la determination de Fe, Mn, Zn, Cu, Pb Cr Al et Cd en sédiments. (In French, with English abstract.). *In* R. Prost (ed.) Contaminated soils. Third Int. Conf. on the Biogeochem. of Trace Elements, Paris [CD-ROM]. 15–19 May 1995. INRA Editions, Paris.

Marley, M.C., and G.E. Hoag. 1986. Induced soil venting for recovery restoration of gasoline hydrocarbons in vadose zone. p. 473–503. *In* Proc. Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, TX. 12–14 Nov. 1986. Natl. Water Well Assoc., Houston.

McKee, K.L., I.A. Mendelssohn, and M.W. Hester. 1988. Reexamination of pore water sulfide concentrations and redox potentials near the aerial roots of *Rhizophora mangle* and *Avicennia germinans*. Am. J. Bot. 75:1352–1359.

Neter, J., W. Wasserman, M.H. Kutner, and C.J. Nachtsheim. 1996. Applied linear statistical models. 4th ed. McGraw-Hill, Irwin, Chicago.

Nyman, J.A. 1999. Effect of crude oil and chemical additives in metabolic activity of mixed microbial population in fresh marsh soils. Microb. Ecol. 37:152–162.

Nyman, J.A., and W.H. Patrick, Jr. 1995. Effects of oil and chemical responses on fresh marsh function and oil degradation: Response implications. Louisiana Oil Spill Coordinator's Office, Office of the Governor, Louisiana Applied Oil Spill Res. and Development Program, Baton Rouge.

Patrick, W.H., R.P. Gambrell, and S.P. Faulkner. 1996. Redox measurement of soils. p. 1225–1273. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI.

Paz González, A., T. Taboada Castro, and M. Taboada Castro. 2000. Levels of heavy metals (Co, Cu, Cr, Ni, Pb and Zn) in agricultural soils of northwest Spain. Commun. Soil Sci. Plant Anal. 21:1773–1783.

Pennings, M. 1987. The influence of column choice and method of integration when determining mineral oil gas chromatographically. ICW Note 1824. Winand Staring Centre, Wageningen, the Netherlands.

Pezeshki, S.R., M.W. Hester, Q. Lin, and J.A. Nyman. 2000. The effects of oil spill and clean up on dominant US Gulf Coast marsh macrophytes: A review. Environ. Pollut. 108:129–139.

Pons, L.J., and N. Van Breemen. 1982. Factors influencing the formation of potential acidity in tidal swamps. p. 35–37. *In* H. Dost and N. Van Breemen (ed.) Proc. of the Bangkok Symp. on Acid Sulphate Soils. 18–24 Jan. 1981. ILRI, Wageningen, the Netherlands.

Referentie Informatiemodel voor Ziekenhuisapotheken. 1980. Quantification of the mineral oil content in extracts from environmental samples: Comparison of various standardized methods. Note 88.040x. RIZA, Lelystad, the Netherlands.

Referentie Informatiemodel voor Ziekenhuisapotheken. 1987. Quantitative determination of mineral oil in watersoil. Note 87.062x. RIZA, Lelystad, the Netherlands.

Roscupp, R.J., and J. Bowman. 1967. Thermal stabilities of vanadium and nickel petroporhyrins. p. 77. *In* Preprints of the Division of Petroleum Chemistry. Am. Chem. Soc., Washington, DC.

Sanders, H.L., S.F. Grassle, Q.R. Hampson, L.S. Morse, S. Garner-Price, and C.C. Jones. 1980. Anatomy of an oil spill: Long term effects from the grounding of the barge Florida off West Falmouth, Massachusetts. J. Mar. Res. 38:265–380.

Stencel, J.R., and P.J. Jaffe. 1998. Trace metal analysis using ion chromatography in water partitioned from crude-oil spills. p. 223–230. *In* R. García and C.A. Brebbia (ed.) Proc. First Int. Conf. on Oil and Hydrocarbon Spills, Modelling Analysis and Control, Southampton, UK. 29–31 July 1998. WIT Press, Southampton, UK.

Wade, T.L. 1993. Oysters as biomonitors of the Apex Barge oil spill. p. 313–317. *In* Proc. of the 1993 Oil Spill Conf., Tampa, FL. 29 Mar.–1 Apr. 1993. Am. Petroleum Inst., Washington, DC.

Walkley, A., and I.A. Black. 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic titration method. Soil Sci. 34:29–38.

Wedepohl, K.H. 2000. The composition of the upper earth's crust and the natural cycles of selected metals. Metals in raw materials. Natural resources. p. 3–19. *In* E. Merian (ed.) Metals and their compounds in the environment. Part I. John Wiley & Sons, New York.

Weisman, W.H. (ed.) 1998. Total petroleum hydrocarbon criteria working group series. Vol. 1. Analysis of petroleum hydrocarbons in environmental media. Amherst Sci. Publ., Amherst, MA.