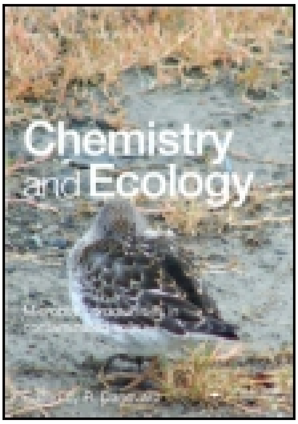

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gche20

Persistence of heavy metals in river sediments

Maria Letizia Ruello [a], Daniela Sani [a], Miriam Sileno [a] & Gabriele Fava [a]

[a] Department FIMET, Università Politecnica delle Marche, Ancona, Italy

To cite this article: Maria Letizia Ruello, Daniela Sani, Miriam Sileno & Gabriele Fava (2011): Persistence of heavy metals in river sediments, Chemistry and Ecology, 27:S1, 13-19

To link to this article: http://dx.doi.org/10.1080/02757540.2010.534985

Chemistry and Ecology
Vol. 27, Supplement, February 2011, 13–19

Persistence of heavy metals in river sediments

Maria Letizia Ruello*, Daniela Sani, Miriam Sileno and Gabriele Fava

Department FIMET, Università Politecnica delle Marche, Ancona, Italy

(*Received 15 January 2010; final version received 22 October 2010*)

The objective of this study was to assess heavy metals accumulation and equilibrium phenomena in river sediment, in relation to water quality, and to assess metals lability, analysing whether and how easily heavy metals are available to generic biota. The diffuse gradient in thin film technique was used to assess the effective concentration (C_E). The solid–liquid distribution coefficient of the metals labile pool (K_{dl}) was calculated to include it in risk analysis within a more realistic frame. The Esino River was chosen for the case study. The results confirmed the need to determine K_d experimentally; values of K_d taken from the literature resulted in errors of some orders of magnitude. Metals speciation, environmental conditions, the type and texture of the sediment, features of the water, organic fraction, pH and salinity can all influence the outcome. The results showed that the two main parameters on which K_d depends are chemical oxygen demand and specific surface area. C_E, which takes into account the contribution of both the water and the labile fraction in the sediment, is a key parameter and may be 5–100× the concentration in the pore water.

Keywords: effective concentration; metals lability; solid–liquid distribution

1. Introduction

In natural waters, gradients in physical, chemical and biological properties are greatest at the sediment–water interface. Dynamic conditions are usually most pronounced at the sediment–water interface where nonsteady-state conditions and steep chemical gradients are frequently encountered. Such processes can cause rapid back-diffusion of released species into the overlying water column or their removal to secondary carrier phases within the sediments. Physical transport systems, such as the resuspension or bioturbation of particles, control the physical boundary conditions for chemical reactions immediately above or below the sediment–water interface [1]. Biogenic, authigenic and mineral particles which settle through the water column are brought to rest at the sediment surface where they accumulate to relatively high concentrations and, compared with their time in the water column, have a long residence time in which to react.

Assessment of the ecological risks posed by heavy metals in an aquatic environment is historically linked to generic quality standards, based on total content in sediment. The European Water Framework Directive [2] aims to assess the risks posed by pollutants in the water phase by taking into account chemical or bio-availability. A better description of the ecological risks

---

*Corresponding author. Email: m.l.ruello@univpm.it

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540.2010.534985
http://www.informaworld.com

is obtained by chemical speciation, which originates from the lability of metal species [3]. The most labile form is the freely dissolved ion, followed by dissolved inorganic metal-ion pairs and organic forms. The concept of the free-ion activity model assumes that the free aqueous metal ion concentration, rather than the total dissolved or sediment concentration, largely determines the toxicological or biological effect observed in organisms exposed to water or sediment containing heavy metals. Although there appear to be exceptions, many studies have demonstrated that a large variety of benthic taxa accumulate metals from the water phase [4–7]. For this reason, understanding the exchange of trace metal between the solid and the solution phases is critical when trying to estimate the risk associated with polluted sediments.

Until recently, most studies have focused on using either a linear distribution coefficient (K_d) or a non-linear adsorption of the metal between the two pools. The importance of the kinetics that control these equilibria has also been recognised, because they can control metal supply to the water phase [8]. A proportion of the metal will only be available from the solid phase if it is capable of rapid transfer into solution. This solid-phase metal is then said to be kinetically labile. Characterisation of these properties may provide an assessment of the potential hazards of a sediment polluted with heavy metals. The technique of diffusive gradient in thin films (DGT) is founded on kinetic rather than equilibrium principles [9,10]. DGT deployment in sediment (and soil) provides information on the metal binding and desorption kinetics which can be interpreted directly as pore water concentration, furthermore it is possible to quantify the mobility of heavy metal cations using a parameter called effective concentration (C_E; $\mathrm{mg \cdot L^{-1}}$).

The aim of this study is to define the key parameters for risk assessment linked to heavy metal contamination of river sediment. The Esino River was chosen as the case study in which routine investigation parameters for assessment of water quality were adopted, along with traditional parameters for the characterisation of sediments and the technique of dynamic speciation.

2. Materials and methods

2.1. *Sites selection and sediment characterisation*

The Esino River basin is located in the middle of the Marche Region. It flows perpendicular to the Adriatic Sea coast, from south-west to north-east. The drainage basin is $\sim$1250 $\mathrm{km^2}$. The river is 75 km long, with an average slope of 1.2% [11] (maximum 1.75% at the river head, minimum 0.35% in the valley). The main water use is for hydroelectric power generation. Consumptive water includes: industrial supplies (91%), agricultural and livestock (6%) and other (3%) [12]. This intensive use of the Esino River justifies the sediment quality investigation.

The study was performed during summer 2008, when the flow rate of the water was very low, 0.42–3 $\mathrm{m^3 \cdot s^{-1}}$. Seven sampling sites were selected along the river (Figure 1). On-site sampling was limited, preferably selecting the deposition zone, and homogenising at least 5–10 samples per zone. The collected sediment was stored in 2 L plastic jars with native water ($\sim$1 L of saturated sediment and 1 L of water supernatant) and taken to the laboratory within a few hours of sampling. All laboratory determinations (including sediment sampling) were conducted according to ASTM requirements [13]. Assessment of the heavy metal accumulation required characterisation of the bed sediment in terms of chemical–physical parameters: granulometry, weight of volume (γt; $\mathrm{kN \cdot m^{-3}}$), specific surface area (SSA; $\mathrm{cm^2 \cdot g^{-1}}$), pH, electrical conductivity (EC; $\mathrm{\mu S \cdot cm^{-1}}$) and mineralogy. Average values of pH and EC, determined on the sediment supernatant, were $\sim$8 and $\sim$700 $\mathrm{\mu S \cdot cm^{-1}}$, respectively. Mineralogical analysis highlighted mainly quartz (SiO_2) and calcite ($CaCO_3$), with a prevalence (of 1–3 times) of calcite over quartz. Sediment granulometry pointed out the prevalence of gravel (ranging from 50 to 60%) and sand (ranging from 30 to 40%). In all samples, the fine fraction (clay) was $<$1.5%, despite the presence of 10% lime. SSA

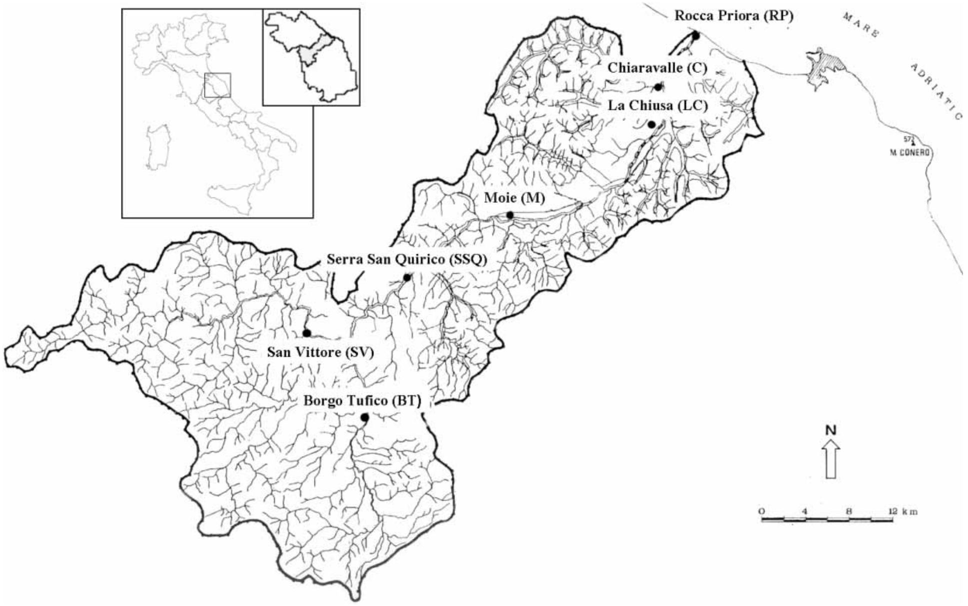

Figure 1. Esino River and its monitoring stations. BT (Borgo Tufico; 12.0° 59.0′ 21.77″ W, 13.0° 0.0′ 6.0″ E, 43.0° 21.0′ 5.82″ N, 43.0° 20.0′ 27.3″ S); SV (San Vittore; 12.0° 57.0′ 58.68″ W, 12.0° 58.0′ 43.0″ E, 43.0° 24.0′ 26.91″ N, 43.0° 23.0′ 48.39″ S); SSQ (Serra San Quirico; 12.0° 58.0′ 17.84″ W, 13.0° 5.0′ 37.0″ E, 43.0° 29.0′ 1.59″ N, 43.0° 22.0′ 44.69″ S); M (Moie; 13.0° 7.0′ 22.24″ W, 13.0° 8.0′ 7.0″ E, 43.0° 30.0′ 26.86″ N, 43.0° 29.0′ 48.34″ S); LC (La Chiusa; 13.0° 19.0′ 20.87″ W, 13.0° 19.0′ 43.0″ E, 43.0° 33.0′ 38.02″ N, 43.0° 33.0′ 18.76″ S); C (Chiaravalle; 13.0° 20.0′ 6.41″ W, 13.0° 20.0′ 51.0″ E, 43.0° 37.0′ 7.18″ N, 43.0° 36.0′ 28.66″ S); RP (Rocca Priora; 13.0° 22.0′ 9.33″ W, 13.0° 22.0′ 31.0″ W, 43.0° 38.0′ 18.75″ N, 43.0° 37.0′ 59.48″ S) [21].

Table 1. Sediment samples physical parameters.

Sample	Gravel (%)	Sand (%)	Lime (%)	Clay (%)	C_u –	C_c –	SSA ($cm^2 \cdot g^{-1}$)	COD ($\mu g\ O_2 \cdot mgTS^{-1}$)	γ_t ($kN \cdot m^{-3}$)
BT	70	28	1.4	0.6	17.2	1.8	3370	4,8	17.7
SV	65	31	3.2	1.3	58.3	1.7	4350	8,1	19.0
SSQ	59	40	0.9	0.1	53.3	0.3	2160	0,4	16.7
M	25	73	1.8	0.2	5.38	1.3	2500	0,5	18.0
LC	58	33	8.2	0.8	92.3	0.2	3090	3,8	17.4
C	52	37	10.6	0.4	66.7	0.4	3210	7,0	16.7
RP	52	37	10.6	0.4	98.3	0.7	4600	11,9	16.7

Note: Saturation degree 100 (–), C_u, coefficient of uniformity; C_c, coefficient of curvature.

follows the clay trend as well as the organic matter content (COD, $\mu g\ O_2 \cdot mg\ TS^{-1}$) [14]. Sediment physical and chemical parameters are listed in Table 1. Consequently, according to the flow of the river, valley sediments (samples LC, C and RP) are more sensitive to heavy metals accumulation, although slight reactivity is present in samples BT and SV, mainly due to the organic fraction.

Total metal content (C_s; $mg \cdot kg^{-1}$) in the fine fraction (<2 mm) was determined by atomic emission spectroscopy (ICP-AES; Perkin–Elmer Optima 3200XL) after aqua regia digestion [15]. The metal concentration in water (C_w; $mg \cdot L^{-1}$) was analysed by atomic absorption spectroscopy (Thermo Electron Corp., M Series AA Spectrometer, GF952 Zeeman Furnace) after filtration (cellulose nitrate membrane filter, 25 mm diameter, 0.45 μm porosity; Schleicher & Schuell, UNIFLO 25\0.45 RC). The solid/liquid partition coefficient (K_d; $L \cdot kg^{-1}$) was obtained as the ratio between C_s and C_w.

2.2. *Metal speciation*

DGT test was performed, taking care to maintain the sediment saturated with its native water during sieving at 2 mm. The excess water was then removed and the DGT device (soil deployment moldings, diffusive gel 0.8 mm thickness, open pore, DGTResearch Ltd., Lancaster) was applied to a sediment paste at 100% saturation. To ensure saturation during testing (i.e. avoiding evaporation), the deployment containers were covered with plastic film, closed in a box (with a water layer at the bottom) and stored at room temperature. After 1, 3 and 5 days, respectively, for each specimen, the mass of metal accumulated on the DGT devise was measured using ICP to calculate the mean concentration of labile metal in the pore water at the interface between the device surface and the sediment [10].

DGT theory introduces the concept of effective concentration (C_E; mg·L^{-1}), which considers the contribution of the pore water concentration and the labile pool dynamically supplied by the solid phase. C_E is calculated using the DGT-induced fluxes in sediments (DIFS) model [16]. DIFS interpolation of the experimental data also provides the partition coefficient for labile species (K_{dl}; L·kg^{-1}) and the characteristic time for the system to approach equilibrium (T_c; s) [17]. In particular, K_{dl} is defined as the ratio between the concentration of the labile pool adsorbed by the solid phase and the metal concentration in water; whereas T_c is the time, characteristic for each metal–sediment system, necessary to restore equilibrium after perturbation by the DGT probe (local depletion of concentration that mimic biota uptake).

C_E, K_{dl} and T_c, calculated as outputs of the DIFS model, are parameters of dynamic metal speciation that allow us to assess the size of the labile pool in the solid phase. DGT deployment at different times (typically 0.5–7 days; in this study 1, 3 and 5 days) is necessary to ensure a more affordable experimental dataset for the DIFS model.

3. Results and discussion

Sediments containing higher percentages of fine-grained fractions and organic matter have a higher specific surface area, and surface processes such as adsorption and adhesion of dissolved and colloidal species are more intense in this type of sediment than in sediments made up of coarse-grained particles [18,19]. Also, the investigated sediment has a total metal content (C_s; Table 2) and solid/liquid partition coefficient (K_d; Table 3) that are directly related to organic matter.

In order to find a relation between the main investigated parameters, simple statistical analysis was performed. The obtained relations allow us to describe C_s and K_d as functions of COD. However, by including SSA in the statistical analysis, the correlation between observed and

Table 2. Total metal content in sediment and water.

	Concentration in sediment (C_s; mg·kg^{-1})					Concentration in water (C_w; µg·L^{-1})				
Sample	Ni	Pb	Cr	Cu	Zn	Ni	Pb	Cr	Cu	Zn
BT	14.5	2.8	10.7	19.5	21.1	2	0.5	6.4	2	10
SV	9.3	0.1	3.6	6.8	13.9	2	0.8	1.0	5	10
SSQ	19.8	2.8	10.9	16.1	20.3	3	0.5	5.0	2	10
M	16.2	1.8	9.7	8.2	16.7	3	0.5	3.0	3	10
LC	14.1	1.8	7.6	13.1	21.5	9	0.5	1.0	5	10
C	27.9	4.0	14.7	16.8	37.3	7	0.5	0.8	5	10
RP	21.3	3.2	13.8	17.6	31.4	5	0.5	0.5	5	10

Table 3. Heavy metal solid/liquid partition coefficients.

	Solid/liquid partition coefficient (K_d; L·kg^{-1})				
Sample	Ni	Pb	Cr	Cu	Zn
BT	7264	5657	1671	9771	2108
SV	4630	128	3600	1362	1388
SSQ	6600	5657	2185	8035	2031
M	5400	3600	3214	2743	1671
LC	1571	3600	7585	2622	2147
C	3985	7971	19542	3368	3728
RP	4268	6428	27514	3522	3137

calculated values was improved, with the following equation:

$$X_y = \alpha + \beta \text{COD} - \eta \text{SSA}.$$

The description of K_d for some metals (Ni, Cu and Cr) may be further improved slightly by including pH and temperature in the statistical analysis.

The results confirmed the need to determine K_d experimentally: the values given in the literature, and widely used in risk analysis, resulted in errors of some orders of magnitude.

The dynamic speciation parameters obtained by DGT are reported in Table 4. The mass of Pb, Cr and Cu accumulated on DGT resin was always below detection limits, except for Cr in sample BT. The effective concentrations in the pore water of the sediment were always much larger than in the river water (up to two orders of magnitude). It is interesting to observe that proportionality between and C_E and C_s or C_w does not exist (Tables 2 and 4). The general trend shows a decrease in C_E and K_{dl} (partition coefficients of the labile species) for increasing values of COD.

The presence of organic matter seems to lead to the formation of metal species in complex forms, able to fix the metal to the solid phase, increasing the persistence of the metal. However, whereas K_d values for Zn and Ni are comparable, K_{dl} values for Ni are generally much larger and its dependence on the organic matter content is more pronounced. In fact, only the SSQ sediment with a low organic matter content and low percentage of clay, shows a similar labile content for Ni and Zn. The main impact on this behaviour is probably due to organic matter with its ability to bind ions chemically (as humic acids) or to form complex compounds. Although it is doubtful whether the presence of clay in the sediment in quantities $<1\%$ significantly affects the mobility of the ions and their distribution between phases. Moreover, for some specimens (M, LC and C), the trend in the mass of Ni accumulated on the DGT resin over time was atypical and did not provide the desorption kinetic parameters (K_{dl} and T_c). This behaviour might be attributed to the presence of metal speciation that cannot be perceived by DGT [20]. Also, regarding T_c values, it is

Table 4. Dynamic speciation parameters C_E, K_{dl} and T_c.

	C_E (µg·L^{-1})			K_{dl} (L·kg^{-1})			T_c (s)		
Sample	Ni	Zn	Cr	Ni	Zn	Cr	Ni	Zn	Cr
BT	229	237	37	2900	200	900	0,1	5	0,5
SV	118	197	–	1900	120	–	30	30	–
SSQ	67	193	–	330	500	–	250	48	–
M	148	199	–	–	467	–	–	43	–
LC	343	220	–	–	220	–	–	1	–
C	38	86	–	–	155	–	–	19	–
RP	71	120	–	530	130	–	300	30	–

possible to observe the effect of organic matter. The sediments from the three sites located in the final part of the basin are very similar in terms of physical parameters, but they have increasing amounts of organic matter: here the amount of labile species of Zn in the solid phase decreases slightly and the response time of the sediment to depletion increases in magnitude. For Ni, small differences in the physical characteristics of the sediment seem to be reflected in large differences in K_{dl} and T_c; the chemistry of the sediment (the type of mineral and organic matter) seems to strongly influence this metal (T_c varies from fractions of seconds to hundreds of seconds).

4. Conclusions

According to routine investigation into parameters linked to heavy metal contamination, the Esino River has good water and sediment quality. The heavy metal concentrations were always well below the quality limit. The sediment shows a buffer capacity toward metals, because the partition coefficient for their labile fraction, as measured by the DGT technique, is below one third of the total metal partition coefficient. Nevertheless the effective concentrations of the free aqueous metal ions are high, if compared with the concentration in the river water. Although, based on the traditional parameter, the river has the same total metal content, the DGT investigation highlighted a vast range of behaviour for metal persistence. Speciation analysis made an important contribution to the risk assessment linked to heavy metal contamination in river sediment. Traditional speciation analysis is difficult and time consuming. The DGT technique seems relatively simple and inexpensive, and can be routinely adopted in conjunction with traditional parameters with the aim of assessing the risks of pollutants in the water phase by allowing chemical or biological availability to be taken into account. The technique can be recommended for sediment characterisation where the evaluation of the risk is strategic for land administration.

References

[1] P. Santschi, P. Höhener, G. Benoit, and M. Buchholtz-ten Brink, *Chemical processes at the sediment–water interface*, Mar. Chem. 30 (1990), pp. 269–315.

[2] *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, Framework for Community Action in the Field of Water Policy*, European Parliament, Brussels, 2000.

[3] J.P.M. Vink, *The origin of speciation: trace metal kinetics over natural water/sediment interfaces and the consequences for bioaccumulation*, Environ. Pollut. 157 (2009), pp. 519–527.

[4] S.V. Lalonde, L.A. Amskold, L.A. Warren, and K.O. Konhauser, *Surface chemical reactivity and metal adsorptive properties of natural cyanobacterial mats from an alkaline hydrothermal spring, Yellowstone National Park*, Chem. Geol. 243 (2007), pp. 36–52.

[5] A. Ciutata, M. Gerinob, N. Mesmer-Dudonsa, P. Anschutzc, and A. Boudoua, *Cadmium bioaccumulation in Tubificidae from the overlying water source and effects on bioturbation*, Ecotoxicol. Environ. Saf. 60 (2005), pp. 237–246.

[6] L. Xie, D. Lambert, C. Martin, D.J. Cain, S.N. Luoma, and D. Buchwalter, *Cadmium biodynamics in the oligochaete* Lumbriculus variegatus *and its implications for trophic transfer*, Aquat. Toxicol. 86 (2008), pp. 265–271.

[7] O. Percevala, B. Pinel-Alloula, G. Methota, Y. Couillardc, A. Giguereb, P.G.C. Campbell, and L. Hare, *Cadmium accumulation and metallothionein synthesis in freshwater bivalves (*Pyganodon grandis*): relative influence of the metal exposure gradient versus limnological variability*, Environ. Pollut. 118 (2002), pp. 5–17.

[8] L. Lesven, Y. Gao, G. Billon, M. Leermakers, B. Ouddane, J.C. Fischer, and W. Baeyens, *Early diagenetic processes aspects controlling the mobility of dissolved trace metals in three riverine sediment columns*, Sci. Total Environ. 407 (2008), pp. 447–459.

[9] W. Davison and H. Zhang, In situ *speciation measurements of trace components in natural waters using. thin-film gels*, Nature 367 (1994), pp. 546–548.

[10] H. Zhang, W. Davison, B. Knight, and S. McGrath, In situ *measurements of solution concentrations and fluxes of trace metals in soils using DGT*, Environ. Sci. Technol. 32 (1998), pp. 704–710.

[11] M. Coltorti and T. Nanni, *Hydrogeology and neotectonics of the lower Esino basin*, Paper of the International Conference on Ground-Water and Man, Sydney, 1983.

[12] Piano di Tutela delle Acque, *Giunta Regionale delle Marche*, Delibera n° 1531 del 18/12/2007, 2007. Available at http://www.regione.marche.it.

[13] *ASTM Book of Standards Volume 4.08: Construction: Soil and Rock (I),* ASTM International, West Conshohocken, PA, 2009.

[14] APAT CNR IRSA 5130 Man 29 2003.

[15] Decreto Ministeriale del 13/09/1999, *Approvazione dei 'Metodi ufficiali di analisi chimica del suolo',* Gazz. Uff. Suppl. Ordin. n° 248 del 21/10/1999.

[16] M.P. Harper, W. Davison, and W. Tych, *One-dimensional views of three-dimensional sediments*, Environ. Sci. Technol. 33 (1999), pp. 2611–2616.

[17] H. Ernstberger, W. Davison, H. Zhang, A. Tye, and S. Young, *Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS*, Environ. Sci. Technol. 36 (2002), pp. 349–354.

[18] N. Vdović, J. Bišćan, and M. Juračić, *Relationship between specific surface area and chemical and physical properties of particulates: study in the northern Adriatic*, Mar. Chem. 36 (1991), pp. 317–328.

[19] I. Ujevic, N. Odzak, and A. Baric, *Trace metal accumulation in different grain size fractions of the sediments from a semi-enclosed bay heavily contaminated by urban and industrial wastewaters*, Water Res. 34 (2000), pp. 3055–3061.

[20] M.L. Ruello, M. Sileno, D. Sani, and G. Fava, *DGT use in contaminated site characterization. The importance of heavy metal site specific behaviour*, Chemosphere 70 (2008), pp. 1135–1140.

[21] Ministry for the Environment, Land and Sea, *Portale Cartografico Nazionale – Ministero dell'Ambiente e della Tutela del Territorio e del Mare*. Available at http://www.pcn.minambiente.it/mdSearch/.