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JANUSZ OSTROWSKI

STUDIES ON THE ADSORPTION AND AVAILABILITY OF PYRAZON

Institute of Organic Industrial Chemistry, Warszawa

Pyrazon (5-amino-4 chloro-2 phenylpyridazin-3(2H)-one; mol-weight — 221,7) is the relatively new soil applied herbicide recommended for the control of weeds in sugar beet.

The amount of pyrazon required to produce a given level of plant response is variable from soil to soil [4, 5, 9, 19]. It is generally accepted that the herbicides leaching downwards in different soils and the availability of herbicides at their site of action in the soil is governed largely by the degree to which they are adsorbed on the soil particles [7, 15, 21]. Unfortunately information on the subject is limited. Studies on the effects of herbicides on the adsorptive complex of soil are also still wanted [20]. The results on the effects of soil environmental factors on the adsorption of pyrazon and the data on the availability of adsorbed pyrazon to plants are lacking. We know nothing about the ultimate fate of many adsorbed herbicides [23].

This report is one in a series which has had as its objective better understanding of the soil sorption and availability of herbicides applied to rooting medium of plants. Previous papers have dealt with herbicides leaching in the soil and their availability in different zones of soil profiles [1, 15], the elimination of herbicides carryover effect by their adsorption on activated carbon [16], the mechanisms of herbicides action [14], and the effect of localized root application of herbicides on their uptake and effectiveness [13].

The investigations reported herein were conducted:

— to determine the degrees of pyrazon adsorption in three different soils and one clay material,

— to evaluate some soil environmental factors affecting pyrazon sorption and activity and

— to get information on the availability of adsorbed pyrazon for uptake by the plants.

MATERIALS AND METHODS

Some series of experiments were conducted studying the adsorption and availability of pyrazon.

The following soils were selected for the examinations: coarse sandy soil from Chylice, sandy loam soil from Chylice and mucky-peat soil (marsh-peat soil) developed from peat soil, taken from Wizna Marsh. Bentonite clay here examined was from Radzionków and had rather polymineral character with greater amount of montmorillonite, probably mixed with various amount of illites [6]. The mechanical analysis and organic matter content of the soils used are given in Table 1. Soils were air-dried and passed through at 1 mm sieve. Pyrazon was used as Pyramin.

In the experiments to study the static adsorption of pyrazon a wet slurry technique was used. The samples of 8 ppm a.i. aqueous solution of pyrazon and the given soil (in 6 : 1 slurry) were rotary shaken in the closed systems for 24 hours. In studies on the adsorption of pyrazon on bentonite — the samples of 8 ppm a.i. pyrazon in water or in 0,01 M $CaCl_2$ (to insure better wetting) and bentonite RM (in 10 : 1 slurry) were shaken as mentioned above. After equilibration the samples were centrifuged and the supernatant solutions were bioassayed.

To determine the effect of temperature on the dynamic adsorption of pyrazon, soil columns filled with sandy loam soil to 3 cm high were prepared and percolated with 8 ppm a.i. aqueous solution of pyrazon.

Table 1

The mechanical analysis and organic matter content of the soils used in different experiments

Soil	Sand 1-0,05 mm	Silt 0,05-0,002 mm	Clay < 0,002 mm	Organic mater
	%			
Coarse sand soil - Ia	88	10	2	0,83
Sandy loam soil - IIIa	66	23	11	2,27
Mucky /marsh/ - peat soil - VI	-	-	-	68,36

The systems were moved to +3°C or to +25°C and allowed to stay there 2 hours before percolation. The effluents were collected and bioassayed.

To study the effect of pH on pyrazon adsorption under shaking conditions (in 4 : 1 slurry), sandy loam soil samples were treated with HCl to give pH values of 4,8 or with $Ca(OH)_2$ to give pH of 11,6. Pyrazon concentration 8 ppm a.i.

To evaluate sandy loam soil saturation limit for pyrazon, the successive increments of an input 8 ppm a.i. aqueous solutions were compared with separately gathered effluents after the percolation through above mentioned soil columns.

To study the availability of adsorbed pyrazon for uptake by the plant, the phytotoxicity of the supernatant and the 4 : 1 slurry after standard rotary shaking was compared (4 ppm a.i. aqueous solution of pyrazon before contact with the soil). In addition the pytotoxicity of saturated sandy loam soil in soil column after careful washing with distilled water was evaluated using quartz sand stratified with this saturated soil. Approximate method of studies on paraquat availability was used by Weber and Scott [22].

White mustard *Sinapis alba* L. bioassays were conducted to determine the adsorption and availability. The samples of 10 ml solutions before and after the contact with the given soil were applied on the surface of the waxed pots filled with quartz sand (0,5 kg air dry sand), previously treated with nutrient solution and seeded with 20 mustard seeds [1]. In the experiments on the availability of adsorbed pyrazon, quartz sand in the pots was stratified with herbicide saturated and washed soil or with the equilibrated slurry, beneath mustards seeds placement. Treatments with supernatants or untreated soil were carried out in analogous way. Such the stratification forced the roots to grow through pyrazon-soil complex layer.

Some two weeks after planting, mustards were cropped at the sand line and the fresh weight determined. Fresh weight index was adopted as it better reflected actual fitocidal action and herbicide concentration in examined solutions.

All treatments were replicated four times.

The results were expressed by fresh weight reduction of bioindicating plants. In some experiments the amount of pyrazon adsorbed was estimated by extrapolation, using the following procedure; percent fresh

[1] Nutrient solution of uniform composition for all treatments was used. It contained 1 g $Ca(NO_3)_2$, 0,25 g K_2HPO_4, 0,25 g $MgSO_4$, 0,12 g KCl and one drop of 5% $FeCl_3$ per 1 liter of water.

weight reduction of the standard, as compared to the control, was plotted against the known concentration of the herbicide, and a courve was drawn to fit the points. The point on the concentration axis, which corresponded to the point of intersection of the curve and the value for fresh weight reduction in individual treatments, was taken as the concentration of pyrazon in the supernatant after the adsorption. In these cases the distribution coefficient (Kd) was adopted [17, 21], which in the ratio of the amount of herbicide adsorbed to the amount unadsorbed, per gram of soil per ml. Kd values were calculated with the following equation [2, 21]:

$$Kd = \frac{\text{ppm of pyrazon in input solution} - \text{ppm in equilibrium solution}}{\text{ppm in equilibrium solution}} \cdot \frac{\text{ml solution}}{\text{g adsorbent}}$$

RESULTS

The influence of soil kind on the static adsorption of pyrazon, as expressed by distribution coefficients (Kd), is shown in Table 2.

Kd value of pyrazon on sandy loam soil was more than three times that on coarse sandy soil, and Kd values of this herbicide on peat soil was more than 37-fold that on coarse sandy soil and more than 12-fold that on sandy loam. The adsorption increased merkedly with increasing organic matter percentage of the soil examined.

The results of pyrazon adsorption on bentonite RM from Radzionków as determined by mustards fresh weight reduction are shown in Table 3.

The phytotoxicity of pyrazon solution was reduced by the contact with bentonite. Clay material, suspended in dilute herbicide solution, adsorbed pyrazon. In additional experiment, coarse sandy soil (pH_{H_2O} —

Table 2

Effect of soil kind on the distribution coefficient /Kd value/ of pyrazon

Soil tested	Kd value
Coarse sandy soil - Ia	0,714
Sandy loam soil - IIIa	2,202
Mucky-peat soil - VI	27,102

Table 3

Effect of bentonite on reducing the phytotoxicity of pyrazon to mustard seedlings

Treatments /adsorbent´s type/	Mustards fresh weight reduction in %
Pyrazon before adsorption	70,8
Bentonite + $CaCl_2$	49,7
Bentonite	54,0

Table 4

Effect of temperature on pyrazon adsorption as expressed by phytotoxicity of the effluents percolated through sandy loam at different temperature

Treatments	Mustard fresh weight reduction in %
Input solution of pyrazon	69,3
Effluent percolated at +3°C	52,8
Effluent percolated at +25°C	58,0

5,6 and pH_{KCl} — 4,4) amended with cation exchange resin adsorbed more pyrazon than unamended soil.

The effect of temperature on the dynamic adsorption of pyrazon on sandy loam, as expressed by comparison of bioindicator fresh weight reduction after treatment with input solution or the effluent is presented in Table 4.

Temperature did not have as great an effect on the dynamic adsorption of pyrazon as was expected.

Studies on the effect of pH on the static adsorption of pyrazon by sandy loam are presented in Table 5.

Increasing the acidity resulted in increased adsorption of pyrazon on sandy loam soil. Adsorption decreased with pH increasing.

Results concerning sandy loam soil saturation limit for pyrazon illustrate Table 6.

Table 5

Effect of soil pH on pyrazon adsorption as expressed by phytotoxicity of herbicide supernatants after equilibration with sandy loam adjusted to given pH

Treatments /adsorbent's type/	Soil pH/H_2O/	Mustards fresh weight reduction in %
Pyrazon before adsorption	-	68,3
Natural soil	7,2	53,9
Soil treated with Ca/OH/$_2$	11,6	65,0
Soil treated with HCl	4,8	45,0

Table 6

The phytotoxicity of separately collected effluents percolated five times through sandy loam column

Number of successive percolation	Mustards fresh weight reduction in %
3	60
4	62
5	63
Input solution	62

The phytotoxicity of the fourth percolate was equal to that of the input solution. Successive increment of an input aqueous solution containing pyrazon led to soil saturation at given concentration of the herbicide.

Studies on the availability of adsorbed pyrazon for uptake by the plant are presented in Tables 7 and 8.

Table 7

The availability of adsorbed pyrazon /after water washing of the saturated soil/

Treatments	Mustards fresh weight reduction in %
Pyrazon - soil complex	14,2
Last portion of washing water	0

Table 8

The availability of adsorbed pyrazon as indicated by phytotoxic effect of soil-aqueous solution slurry and supernatant

Treatments	Mustards fresh weight reduction in %
Supernatant	46,3
Slurry	59,1

Bioassay results indicated that pyrazon — sandy loam soil complex (carefully washed with distilled water) exerted some bioactivity, when placed in the assay medium, although the last portion of aqueous washing percolate induced no phytotoxicity.

In addition the bioassay of soil-aqueous solution slurry, was conducted and compared directly with equal volumes of the supernatants.

Higher biological activity of the slurry was noted indicating a supposed release of active pyrazon from the pyrazon-soil complex in the presence of mustards roots in the bioassay. The same trend was noted in repeated study with higher concentration of pyrazon. The obtained results suggest that adsorbed pyrazon was available to mustard plants (at least in part).

Special treatments indicated no side effect of natural and modified soils or bentonites supernatants and effluents (without herbicide) on bioindicating material.

DISCUSSION

The effectiveness of the herbicide depends upon the extent to which it can be concentrated in available form in the region of the soil in which its effects are desired. Transport of the herbicide in the soil water, its diffusion through the soil and coming into contact with the herbicide, as the root grows the soil, are the most probable means available to growing plant root for obtaining soil applied herbicide. The movement and adsorption of herbicides in soils, therefore, are of great importance.

It is possible to determine herbicide in aqueous solution, after the contact with soil, by the use of chemical, physicochemical or biological methods. As biological material, in this instance the higher plants, showed a particularly sensitive reaction to pyrazon, the biological method deserved preference over the chemical method. The amount of herbicide in the soil, that is available for uptake, is best measured by the plant itself. Eshel and Warren [3] determined soil adsorption of 2,4-D, amiben, chloropropham and trifluralin in different soils by a method based on cucumber or sorghum root bioassay, which appeared sensitive and suitable for herbicides affecting root growth. Ostrowski [16] evaluated dynamic and static adsorption of diuron and simazine by the soil amended with activated carbon, using white mustard as the bio-indicator.

The studies reported herein demonstrated, that biological methods are of great value to determine the adsorption and availability.

The activity of an adsorbent depends upon its surface area, the accessibility to that surface, and the chemical nature of the surface. Soils including more organic matter and clay minerals usually adsorb more chemicals [3, 7, 21]. Peat soil, in our studies, included 66,09% more organic matter than sandy loam soil, and 67,53% more o.m. than coarse sandy soil. As was found in these studies, soil kind determined the degrees of pyrazon adsorption. There is much evidence, that soil organic matter plays essential role in restriction of pyrazon phytotoxicity by adsorption. Perhaps, in the presence of water, organic matter provides more important sites for the adsorption of pyrazon by soils. Organic matter content with its permutoidal structure and high adsorptive capacity is rather the most influential soil property affecting the activity of this herbicide, but under field conditions, the effect of climatic factors, such as rainfall, temperature and light intensity, must also be considered. Ostrowski [15] indicated that pyrazon leached more readily in the same coarse sandy soil than in sandy loam, richer in organic matter. Lush and Mayes [2] reported that the activity of pyrazon on peat soil was negligible.

Clay lattice structure of montmorillonite is opened by swelling in water [10], and large organic molecules can be accommodated in the lattice of clay mineral, though perhaps not so easily as small elementary cations. Law and Kunze [8] noted, that large organic molecules of another compound of 660,9 molecular weight were held in the interlayer spaces of montmorillonite. After all, a fraction of macromolecule can be in adsorbed state [18]. It would appear that adsorption of pyrazon was lower on hydrophilic clay material than on less hydrophilic soil organic fraction. In interpreting data on pyrazon adsorption by bentonite from Radzinków, one should take into consideration the fact of possible content of organic matter in this clay material [6].

Pyrazon molecule contains nitrogen and oxygen atoms with free electron pairs, and therefore theoretically can be adsorbed by bonding to end-groups of organic matter components polar active in nature, and by hydrogen bonding to oxygen — rich soil particles surfaces. Adsorption of protonated pyrazon forms should be also taken into consideration.

Temperature did not have as great an effect on adsorption as was expected. It may be that the organic matter of the soil caused a moderating effect on the temperature — adsorption relationship. Talbert and Fletchall [21] found, that temperature had a greater effect on the adsorption of simazine than of atrazine.

The adsorption of pyrazon varied with changing pH. Different mechanisms could be operating here to various degrees. Perhaps the activity of end groups of the compounds is changed under different pH conditions. The pH effect may be a result of the differences caused by the saturating cation (hydrogen versus calcium) on the exchange complex, pyrazon probably is able to become ionic decreased pH but the speculation is risky. If this inverse relationship between adsorption and pH occurs in the soil under field condition, then the rate of pyrazon should be increased as the pH of the soil decreased. Fortunately optimum growing conditions for sugar beet are on neutral soils.

The amount of pyrazon found in effluents from soil columns is certainly the result of many processes and conditions (e.g. solubilization, adsorption and hydrodynamic dispersion). To determine the soil saturation limit for pyrazon, successive increments of aqueous solutions were introduced into the top of the column. When a certain amount of the solution has passed through the soil, the break-through point was reached and pyrazon passed to the effluent. After a certain time of filtration the soil became saturated with pyrazon and the herbicide solution passed unchanged through the columns.

In working with saturated soil, the author found, that careful percolation with distilled water (washing) could remove all unbound or loosely bound pyrazon from the soil. Pyrazon retained more tightly by sandy loam soil, appeared to be available to mustard plants (rather in part). The comparison of slurry and supernatants' phytotoxicity permits to draw out analogous conclusions. It was possible to test this working hypothesis, even that pyrazon applied to one-third of the roots gives limited biological responses to the plant [13]. Perhaps root exudates are effective in replacing pyrazon from soil colloids, or the herbicide becomes available by indirect way. Probably different plant species have diverse ability to overcome the fixation strength of herbicides on soil particles, and the release of herbicides fixed by different soil sorbents is unequal. Biassay showed that EPTC-montmorillonite complexes exerted herbicidal activity against germination and growth of rye grass [11]. Paraquat was adsorbed on the surface of the kaolinitic clay and slowly became available to cucumber plants, but when it was adsorbed in the interlayer spacings of montmorillonite clay, it was not available to the plants [22]. For comparison, plants are able to take up adsorbed phosphate, but the mechanism of such the uptake is not completely understood [12]. However soil adsorption had significant regulating effect on pyrazon availability and phytotoxicity. In addition, the adsorption of pyrazon influenced the distribution of this herbicide within the soil [15], and hence its influence on roots and underground portion of the stems of weed or crop plants.

Knowledge of the mechanisms by which herbicides are adsorbed, stored, released, leached in the soil, and taken by the plants, can contribute towards the more efficient and economic use of these compounds, and would also indicate ways in which unwanted side affects and carryover effects might be anticipated and corrected.

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J. OSTROWSKI

BADANIA NAD ADSORPCJĄ I DOSTĘPNOŚCIĄ PYRAZONU

Instytut Przemysłu Organicznego

Streszczenie

Przeprowadzono doświadczenia w celu:

— uzyskania danych o adsorpcji pyrazonu (5 amino-4-chloro-2-fenylopirydaz-3(2H)-onu) przez piasek słabo gliniasty, glinę lekką, glebę .murszowo-torfową oraz bentonit,

— oceny niektórych czynników środowiska glebowego wpływających na adsorpcję i aktywność pyrazonu oraz

— uzyskania informacji o dostępności zaadsorbowanego pyrazonu dla roślin gorczycy.

Rodzaj gleby określał stopień adsorpcji herbicydu. Substancja organiczna gleby odgrywała zasadniczą rolę w ograniczaniu fitotoksyczności pyrazonu w drodze adsorpcji. Zmiana takich warunków doświadczalnych jak pH i temperatura wpływała na adsorpcję pyrazonu przez glebę. Kolejne zwiększanie objętości wcieku w postaci wodnego roztworu pyrazonu prowadziło do wysycenia gleby przy danym stężeniu herbicydu.

Stopień adsorpcji modyfikował dostępność pyrazonu dla roślin i jego aktywność, lecz uzyskane wyniki sugerują, że zaadsorbowany pyrazon jest przynajmniej częściowo dostępny dla roślin gorczycy.

Sorpcja glebowa ma podstawowe znaczenie dla zrozumienia zachowania się i losów pyrazonu w glebie.

Zastosowano biotesty gorczycy białej *Sinapis alba* L. w celu określania adsorpcji i dostępności pyrazonu.

Я. ОСТРОВСКИ

ИССЛЕДОВАНИЯ ПО АДСОРБЦИИ И ДОСТУПНОСТИ ПИРАЗОНА

Институт Органической Промышленности

Резюме

Были проведены исследования для:

— получения данных по адсорбции пиразона (1-фенил-4-амино-5-хлор-пиридазон-6) глинистым песком, легким суглинком, болотно-торфяной почвой и бентонитом,

— оценки некоторых факторов почвенной среды влияющих на адсорбцию и активность пиразона, а также

— получения сведений об доступности для усвоения адсорбированного пиразона растениями белой горчицы.

Степень адсорбции определялась качеством почвы. Органическое вещество почвы играет основную роль в ограничении фитотоксичности пиразона путем адсорбции. Изменение таких опытных условий как pH и температура влияет на адсорбцию пиразона почвой.

Очередное увеличение объема вводимой жидкости в виде водного раствора пиразона приводило к насыщению почвы при заданной концентрации гербицида.

Доступность пиразона для усвоения растением и его активность зависят от его степени адсорбции почвой, но полученные результаты указывают, что даже адсорбированный пиразон оказывается хотя бы частично доступным например для растений горчицы.

Почвенная адсорбция играет основную роль в понимании вопроса действия и судьбы пиразона в почве.

В опытах применялись биотесты на горчицы белой для определения адсорбции и доступности пиразона.

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